Supporting Information

Transition-metal-free direct C-3 cyanation of quinoxalin-2(1*H*)-ones with ammonium thiocyanate as the "CN" Source

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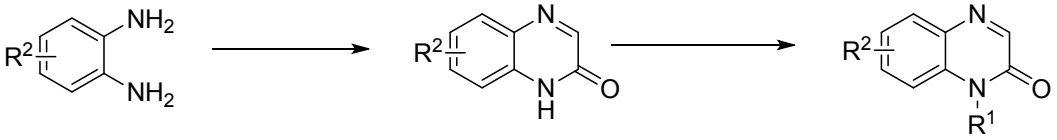
Table of Contents

1. General consideration

All reactions were run in an oven-dried reaction tube at room temperature in air. All reagents were purchased from commercial source and without prior purification. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR were recorded at 400 MHz, 100 MHz and 376 MHz, respectively, using TMS as internal standard. Chemical shifts (δ) are reported in ppm and coupling constants (J) in hertz (Hz). Melting points were determined using a digital melting point apparatus and uncorrected. Mass spectra were measured with a HRMS-ESI instrument or ESI instrument.

2. Preparation of substrates[1]

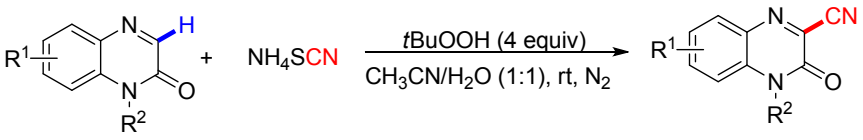


1' **1**

To a dried round-bottom flask charged with a magnetic stirring bar, *o*-phenylenediamine (5 mmol), ethyl 2-oxoacetate (6 mmol) and ethanol (20 mL) were added successively and the mixture was stirred at reflux for 1 h. After completion of the reaction, the reaction mixture was filtered, washed with ethanol and then dried to give quinoxalinone **1'**. Subsequently, a 50 mL oven-dried reaction vessel equipped with a magnetic stirrer bar was charged with quinoxalinone **1'**, potassium

carbonate (1.2 equiv.), corresponding halogenoalkane (1.6 equiv.) and DMF (20 ml). The resulting solution was stirred in air at room temperature overnight. Then the reaction mixture was diluted with ethyl acetate, washed with water, and the organic layer was separated and dried over anhydrous $MgSO_4$. The solvent was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel to afford the desired substrate **1**.

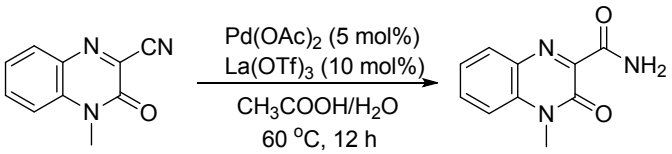
3. Representative procedure for the model reaction



1 **2** **3**

A 10 mL round-bottom flask was charged with quinoxalin-2(1*H*)-ones **1** (0.3 mmol) and the ammonium thiocyanate **2** (0.9 mmol) under N_2 atmosphere. Then, aqueous *t*BuOOH (70% solution in water, 1.2 mmol) in 2 ml of CH_3CN/H_2O (1:1) was added successively by syringe over a period of 10 min, and the resulting solution was stirred at room temperature for 30h. After completion of the reaction, water (20 mL) was added into the reaction mixture, and the resulting mixture was extracted with CH_2Cl_2 (3 × 5 mL). The combined organic layers were dried over $MgSO_4$, filtered, and then concentrated in vacuum. The residue was purified by flash chromatography on silica gel to afford the corresponding product **3**.

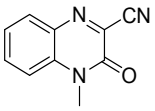
4. Synthetic applications of 3aa



3aa **4 (72%)**

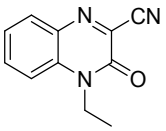
$Pd(OAc)_2$ (3.4 mg, 0.015 mmol) and $La(OTf)_3$ (18.6 mg, 0.03 mmol) were dissolved in acetic acid (2 mL) in a flame-dried Schlenk tube with a magnetic stirring bar, and then 4-methyl-3-oxo-3,4-dihydroquinoxaline-2-carbonitrile **3aa** (55.5 mg, 0.3 mmol) and water(1 mL) were sequentially added. The resulting solution was stirred at 30°C for 12 h. After completion of the reaction, the reaction mixture was diluted with ethyl acetate, then washed with saturated $NaHCO_3$ (2 × 10 mL) and brine (1 × 10 mL). The organic layer was collected, dried over anhydrous $MgSO_4$, and evaporated under vacuum. The residue was purified by column chromatography on silica gel to afford the desired product **4**.

5. Characterization Data for the Products



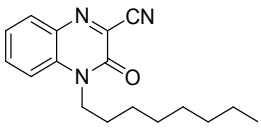
4-methyl-3-oxo-3,4-dihydroquinoxaline-2-carbonitrile (3aa)[2]

Purified by column chromatography (petroleum ether/ethyl acetate = 8:1), light yellow solid, 40 mg, yield 72%; m.p. 163-165°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.0 Hz, 1H), 7.80 (t, *J* = 7.6 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.44 (d, *J* = 8.4 Hz, 1H), 3.79 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.93 (s), 134.73 (s), 134.08 (s), 133.72 (s), 132.92 (s), 131.87 (s), 124.99 (s), 114.29 (s), 114.05 (s), 29.78 (s). IR (cm^{-1}): 775, 1208, 1469, 1533, 1603, 1671, 2235, 3079. HRMS: $C_{10}H_8N_3O$ $[M+H]^+$; found: 186.0650, calculated: 186.0652.



4-ethyl-3-oxo-3,4-dihydroquinoxaline-2-carbonitrile (3ab)[2]

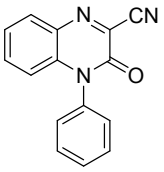
Purified by column chromatography (petroleum ether/ethyl acetate = 10:1), light yellow solid, 42 mg, yield 70%; m.p. 168-170 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.4 Hz, 1H), 7.86 – 7.73 (m, 1H), 7.48 (dd, *J* = 8.0, 6.0 Hz, 2H), 4.38 (q, *J* = 7.2 Hz, 2H), 1.42 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.51 (s), 134.81 (s), 133.61 (s), 133.18 (s), 133.12 (s), 132.01 (s), 124.84 (s), 114.21 (s), 114.15 (s), 38.28 (s), 12.36 (s). IR (cm^{-1}): 744, 1195, 1227, 1449, 1466, 1530, 1604, 1668, 2233, 2988. HRMS: $C_{11}H_9N_3NaO$ $[M+Na]^+$; found: 200.0820, calculated: 200.0818.



4-octyl-3-oxo-3,4-dihydroquinoxaline-2-carbonitrile (3ac)

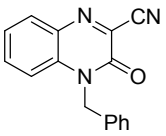
Purified by column chromatography (petroleum ether/ethyl acetate = 15:1), light yellow solid, 58

mg, yield 68%; m.p. 62-64 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.1 Hz, 1H), 7.86 – 7.66 (m, 1H), 7.54 – 7.37 (m, 2H), 4.46 – 4.11 (m, 2H), 1.78 (dt, *J* = 15.6, 7.6 Hz, 2H), 1.56 – 1.18 (m, 10H), 0.89 (t, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.70 (s), 134.60 (s), 133.71 (s), 133.37 (s), 133.18 (s), 132.03 (s), 124.74 (s), 114.29 (s), 114.12 (s), 43.17 (s), 31.73 (s), 29.19 (s), 29.11 (s), 27.23 (s), 26.89 (s), 22.60 (s), 14.08 (s). IR (cm^{-1}): 766, 1811, 1466, 1533, 1603, 1666, 2238, 2850, 2920, 2953, 3068. HRMS: $C_{17}H_{22}N_3O$ $[M+H]^+$; found: 284.1770, calculated: 284.1767.



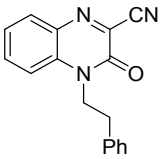
3-oxo-4-phenyl-3,4-dihydroquinoxaline-2-carbonitrile (3ad)[2]

Purified by column chromatography (petroleum ether/ethyl acetate = 12:1), light yellow solid, 44 mg, yield 59%; m.p. 196-198 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.01 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.75 – 7.60 (m, 4H), 7.48 (ddd, *J* = 8.4, 7.6, 3.2 Hz, 3H), 6.70 – 6.63 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 153.13 (s), 135.69 (s), 135.32 (s), 135.24 (s), 134.78 (s), 132.80 (s), 131.01 (s), 130.77 (s), 130.29 (s), 128.63 (s), 125.05 (s), 116.25 (s), 115.34 (s). IR (cm^{-1}): 694, 754, 1303, 1387, 1463, 1490, 1591, 1603, 1621, 1671, 2231, 2931, 3068, 3276. HRMS: $C_{15}H_{10}N_3O$ $[M+H]^+$; found: 248.0816, calculated: 248.0818.



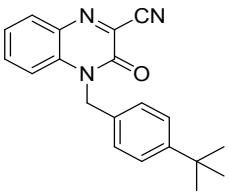
4-benzyl-3-oxo-3,4-dihydroquinoxaline-2-carbonitrile (3ae)

Purified by column chromatography (petroleum ether/ethyl acetate = 12:1), yellow solid, 56 mg, yield 72%; m.p. 174-176 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.74 – 7.62 (m, 1H), 7.51 – 7.24 (m, 7H), 5.55 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.14 (s), 134.71 (s), 134.03 (s), 133.84 (s), 133.46 (s), 133.21 (s), 131.98 (s), 129.18 (s), 128.28 (s), 127.07 (s), 125.03 (s), 115.09 (s), 114.09 (s), 46.60 (s). IR (cm^{-1}): 464, 699, 739, 746, 1179, 1220, 1464, 1532, 1602, 1667, 2234, 2964, 3050. HRMS: $C_{16}H_{11}N_3NaO$ $[M+Na]^+$; found: 284.0796, calculated: 284.0794.



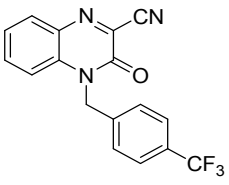
3-oxo-4-phenethyl-3,4-dihydroquinoxaline-2-carbonitrile (3af)

Purified by column chromatography (petroleum ether/ethyl acetate = 12:1), light yellow solid, 63 mg, yield 76%; m.p. 178-180 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.0 Hz, 1H), 7.77 (t, *J* = 8.0 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.41 (d, *J* = 8.4 Hz, 1H), 7.38 – 7.25 (m, 5H), 4.59 – 4.39 (m, 2H), 3.08 (dd, *J* = 9.2, 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.60 (s), 136.89 (s), 134.64 (s), 133.71 (s), 133.28 (s), 133.11 (s), 132.12 (s), 128.94 (s), 128.77 (s), 127.24 (s), 124.85 (s), 114.07 (s), 114.02 (s), 44.47 (s), 33.26 (s). IR (cm^{-1}): 534, 704, 749, 1174, 1207, 1465, 1531, 1604, 1664, 2237, 2971, 3020. HRMS: $C_{17}H_{13}N_3NaO$ $[M+Na]^+$; found: 298.0949, calculated: 298.0951.



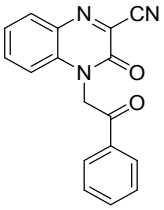
4-(4-(*tert*-butyl)benzyl)-3-oxo-3,4-dihydroquinoxaline-2-carbonitrile (3ag)

Purified by column chromatography (petroleum ether/ethyl acetate = 12:1), yellow solid, 64 mg, yield 67%; m.p. 170-172 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.69 (ddd, *J* = 8.8, 7.2, 1.6 Hz, 1H), 7.44 (dd, *J* = 12.8, 4.8 Hz, 2H), 7.40 – 7.33 (m, 2H), 7.24 (d, *J* = 8.4 Hz, 2H), 5.51 (s, 2H), 1.30 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.11 (s), 151.38 (s), 134.58 (s), 133.94 (s), 133.59 (s), 133.21 (s), 131.94 (s), 130.97 (s), 126.94 (s), 126.06 (s), 124.88 (s), 115.11 (s), 114.07 (s) ,46.30 (s), 34.57 (s), 31.23 (s). IR (cm^{-1}): 768, 1216, 1468, 529, 1600, 1652, 2227, 2966. HRMS: $C_{20}H_{20}N_3O$ $[M+H]^+$; found: 318.1600, calculated: 318.1601.



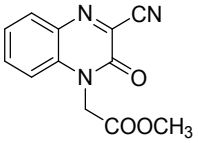
3-oxo-4-(4-(trifluoromethyl)benzyl)-3,4-dihydroquinoxaline-2-carbonitrile (3ah)

Purified by column chromatography (petroleum ether/ethyl acetate = 12:1), yellow solid, 71 mg, yield 72%; m.p. 188-190 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.70 (ddd, *J* = 8.8, 7.2, 1.6 Hz, 1H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.52 – 7.44 (m, 1H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 1H), 5.60 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.00 (s), 138.01 (s), 134.83 (s), 133.86 (s), 133.20 (d, *J* = 1.1 Hz), 132.23 (s), 130.67 (q, *J* = 32.7 Hz), 123.75 (q, *J* = 270.6 Hz), 127.41 (s), 126.19 (q, *J* = 3.8 Hz), 125.26 (s), 114.65 (s), 113.88 (s), 46.13 (s); ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.77 (s). IR (cm^{-1}): 759, 766, 1068, 1115, 1173, 1217, 1326, 1464, 1532, 1602, 1659, 2232, 3105. HRMS: $C_{17}H_{11}F_3N_3O$ $[M+H]^+$; found: 330.0857, calculated: 330.0849.



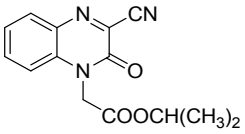
3-oxo-4-(2-oxo-2-phenylethyl)-3,4-dihydroquinoxaline-2-carbonitrile (3ai)

Purified by column chromatography (petroleum ether/ethyl acetate = 12:1), light yellow solid, 66 mg, yield 76%; m.p. 232-234 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.17 (d, *J* = 7.5 Hz, 2H), 8.03 (d, *J* = 7.5 Hz, 1H), 7.80 (dd, *J* = 15.5, 7.5 Hz, 2H), 7.71 – 7.61 (m, 3H), 7.54 (t, *J* = 7.6 Hz, 1H), 6.02 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 191.97 (s), 153.10 (s), 135.33 (s), 134.92 (s), 134.62 (s), 134.46 (s), 133.67 (s), 132.85 (s), 131.43 (s), 129.46 (s), 128.92 (s), 125.39 (s), 116.17 (s), 115.10 (s), 50.08 (s). IR (cm^{-1}): 564, 689, 761, 1000, 1184, 1220, 1234, 1465, 1533, 1602, 1662, 1691, 2235, 2948, 3045. HRMS: $C_{17}H_{12}N_3O_2$ $[M+H]^+$; found: 290.0923, calculated: 290.0924.



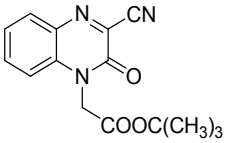
methyl 2-(3-cyano-2-oxoquinoxalin-1(2*H*)-yl)acetate (3aj)

Purified by column chromatography (petroleum ether/ethyl acetate = 15:1), yellow solid, 58 mg, yield 80%; m.p. 172-174 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.81 – 7.71 (m, 1H), 7.51 (dd, *J* = 11.2, 4.0 Hz, 1H), 7.20 (d, *J* = 8.4 Hz, 1H), 5.09 (s, 2H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.57 (s), 152.47 (s), 134.96 (s), 133.56 (s), 133.20 (s), 132.99 (s), 132.20 (s), 125.30 (s), 113.77 (s), 53.24 (s), 43.73 (s). IR (cm^{-1}): 758, 769, 1113, 1185, 1228, 1366, 1424, 1468, 1537, 1604, 1671, 1736, 2238, 2958, 3014. HRMS: $C_{12}H_9N_3NaO_3$ $[M+Na]^+$; found: 266.0548, calculated: 266.0546.



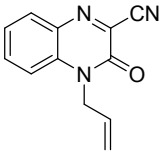
isopropyl 2-(3-cyano-2-oxoquinoxalin-1(2*H*)-yl)acetate (3ak)

Purified by column chromatography (petroleum ether/ethyl acetate = 15:1), yellow solid, 67 mg, yield 82%; m.p. 140-142 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.83 – 7.69 (m, 1H), 7.50 (dd, *J* = 11.2, 4.0 Hz, 1H), 7.17 (d, *J* = 8.4 Hz, 1H), 5.13 (m, 1H), 5.05 (s, 2H), 1.29 (d, *J* = 6.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.55 (s), 152.48 (s), 134.79 (s), 133.63 (s), 133.30 (s), 132.98 (s), 132.17 (s), 125.19 (s), 113.80 (s), 113.77 (s), 70.75 (s), 44.05 (s), 21.71 (s). IR (cm^{-1}): 766, 1109, 1187, 1223, 1374, 1465, 1536, 1603, 1672, 1741, 2238, 2977. HRMS: $C_{14}H_{13}N_3NaO_3$ $[M+Na]^+$; found: 294.0863, calculated: 294.0849.



***tert*-butyl 2-(3-cyano-2-oxoquinoxalin-1(2*H*)-yl)acetate (3al)**

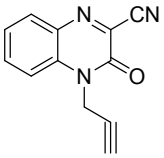
Purified by column chromatography (petroleum ether/ethyl acetate = 15:1), yellow solid, 75 mg, yield 88%; m.p. 172-174 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.0 Hz, 1H), 7.80 – 7.72 (m, 1H), 7.49 (t, *J* = 7.6 Hz, 1H), 7.18 (d, *J* = 8.4 Hz, 1H), 4.98 (s, 2H), 1.49 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.01 (s), 152.49 (s), 134.75 (s), 133.62 (s), 133.36 (s), 132.95 (s), 132.11 (s), 125.13 (s), 113.81 (s), 84.06 (s), 44.51 (s), 27.97 (s). IR (cm^{-1}): 778, 1152, 1218, 1240, 1366, 1467, 1532, 1604, 1667, 1739, 2241, 2973. HRMS: $C_{15}H_{15}N_3NaO_3$ $[M+Na]^+$; found: 308.1019, calculated: 308.1016.



4-allyl-3-oxo-3,4-dihydroquinoxaline-2-carbonitrile (3am)

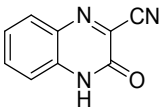
Purified by column chromatography (petroleum ether/ethyl acetate = 10:1), light yellow solid, 42 mg, yield 66%; m.p. 124-126 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.80

– 7.72 (m, 1H), 7.52 – 7.45 (m, 1H), 7.42 (d, *J* = 8.4 Hz, 1H), 6.08 – 5.87 (m, 1H), 5.36 (d, *J* = 10.4 Hz, 1H), 5.24 (d, *J* = 17.2 Hz, 1H), 4.97 (dd, *J* = 3.6, 1.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.55 (s), 134.63 (s), 133.77 (s), 133.37 (s), 133.08 (s), 131.93 (s), 129.47 (s), 124.96 (s), 119.28 (s), 114.85 (s), 114.01 (s), 45.16 (s). IR (cm^{-1}): 765, 773, 1186, 1223, 1467, 1534, 1601, 1656, 2237, 3080. HRMS: $C_{12}H_9N_3NaO$ $[M+Na]^+$; found: 234.0647, calculated: 234.0638.



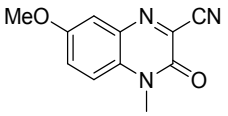
3-oxo-4-(*prop*-2-yn-1-yl)-3,4-dihydroquinoxaline-2-carbonitrile (3an)

Purified by column chromatography (petroleum ether/ethyl acetate = 10:1), light yellow solid, 36 mg, yield 57%; m.p. 173-175 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.0 Hz, 1H), 7.83 (t, *J* = 8.0 Hz, 1H), 7.60 (d, *J* = 8.4 Hz, 1H), 7.53 (t, *J* = 7.6 Hz, 1H), 5.11 (d, *J* = 2.4 Hz, 2H), 2.38 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.93 (s), 134.82 (s), 133.61 (s), 133.11 (s), 132.54 (s), 132.03 (s), 125.34 (s), 114.86 (s), 113.78 (s), 75.49 (s), 74.43 (s), 32.20 (s). IR (cm^{-1}): 762, 1183, 1221, 1466, 1536, 1604, 1668, 2122, 2235, 3243. HRMS: $C_{12}H_7N_3NaO$ $[M+Na]^+$; found: 232.0478, calculated: 232.0481.



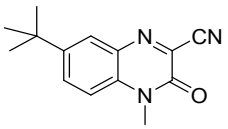
3-oxo-3,4-dihydroquinoxaline-2-carbonitrile (3ao)

Purified by column chromatography (petroleum ether/ethyl acetate = 8:1), yellow solid, 30 mg, yield 58%; m.p. 284-286 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.15 (s, 1H), 7.87 (d, *J* = 8.2 Hz, 1H), 7.80 – 7.67 (m, 1H), 7.46 – 7.34 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 153.66 (s), 135.66 (s), 134.65 (s), 133.54 (s), 132.35 (s), 130.20 (s), 124.84 (s), 116.61 (s), 115.34 (s). IR (cm^{-1}): 595, 762, 886, 1166, 1228, 1607, 1673, 2234, 2891, 3115. HRMS: $C_9H_6N_3O$ $[M+H]^+$; found: 172.0512, calculated: 172.0505.



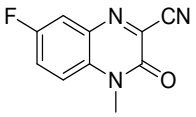
7-methoxy-4-methyl-3-oxo-3,4-dihydroquinoxaline-2-carbonitrile (3ba)[2]

Purified by column chromatography (petroleum ether/ethyl acetate = 10:1), light yellow solid, 43 mg, yield 67%; m.p. 185-187 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (dd, *J* = 9.2, 2.8 Hz, 1H), 7.36 (m, 2H), 3.93 (s, 3H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.76 (s), 152.74 (s), 133.86 (s), 133.74 (s), 128.63 (s), 124.88 (s), 115.18 (s), 114.21 (s), 111.81 (s), 55.96 (s), 29.92 (s). IR (cm^{-1}): 430, 501, 668, 827, 1026, 1173, 1197, 1262, 1372, 1496, 1533, 1644, 1673, 2233, 2840, 2939, 3088. HRMS: $C_{11}H_9N_3NaO_2$ $[M+Na]^+$; found: 238.0581, calculated: 238.0587.



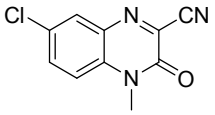
7-(*tert*-butyl)-4-methyl-3-oxo-3,4-dihydroquinoxaline-2-carbonitrile (3bb)[2]

Purified by column chromatography (petroleum ether/ethyl acetate = 8:1), light yellow solid, 52 mg, yield 72%; m.p. 190-192 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 2.0 Hz, 1H), 7.85 (dd, *J* = 8.5, 2.4 Hz, 1H), 7.38 (d, *J* = 8.8 Hz, 1H), 3.77 (s, 3H), 1.41 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.00 (s), 148.57 (s), 133.34 (s), 132.94 (s), 132.80 (s), 131.87 (s), 127.88 (s), 114.23 (s), 114.00 (s), 34.58 (s), 31.08 (s), 29.73 (s). IR (cm^{-1}): 643, 838, 1200, 1228, 1424, 1534, 1573, 1654, 1667, 2235, 2903, 2958, 3088. HRMS: $C_{14}H_{15}N_3NaO$ $[M+Na]^+$; found: 264.1103, calculated: 264.1107.



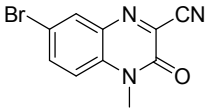
7-fluoro-4-methyl-3-oxo-3,4-dihydroquinoxaline-2-carbonitrile (3bc)[2]

Purified by column chromatography (petroleum ether/ethyl acetate = 8:1), yellow solid, 32 mg, yield 53%; m.p. 183-184 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (dd, *J* = 8.0, 2.8 Hz, 1H), 7.56 (ddd, *J* = 10.4, 7.6, 2.8 Hz, 1H), 7.43 (dd, *J* = 9.2, 4.4 Hz, 1H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.05 (d, *J* = 247.6 Hz), 152.53 (s), 135.19 (s), 133.22 (d, *J* = 11.5 Hz), 130.87 (d, *J* = 2.0 Hz), 122.84 (d, *J* = 24.4 Hz), 116.77 (d, *J* = 22.6 Hz), 115.69 (d, *J* = 8.6 Hz), 113.75 (s), 30.11 (s); ^{19}F NMR (376 MHz, $CDCl_3$) δ -116.15 (s). IR (cm^{-1}): 506, 661, 830, 1193, 1261, 1458, 1488, 1536, 1667, 2228, 3071. HRMS: $C_{10}H_7FN_3O$ $[M+H]^+$; found: 204.0577, calculated: 204.0568.



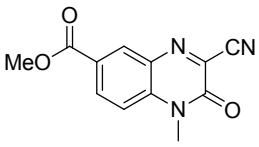
7-chloro-4-methyl-3-oxo-3,4-dihydroquinoxaline-2-carbonitrile (3bd)[2]

Purified by column chromatography (petroleum ether/ethyl acetate = 8:1), yellow solid, 37 mg, yield 56%; m.p. 193-195 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.07 (d, *J* = 2.4 Hz, 1H), 7.90 (dd, *J* = 9.2, 2.4 Hz, 1H), 7.73 (d, *J* = 9.2 Hz, 1H), 3.65 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 153.22 (s), 135.64 (s), 134.40 (s), 133.89 (s), 133.22 (s), 129.75 (s), 128.93 (s), 117.86 (s), 115.14 (s), 30.30 (s). IR (cm^{-1}): 592, 832, 1099, 1197, 1427, 1534, 1598, 1667, 2237, 3071. $C_{10}H_7ClN_3O$ $[M+H]^+$; found: 220.0268, calculated: 220.0272.



7-bromo-4-methyl-3-oxo-3,4-dihydroquinoxaline-2-carbonitrile (3be)[2]

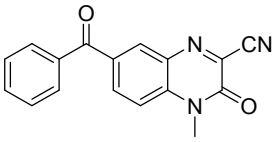
Purified by column chromatography (petroleum ether/ethyl acetate = 8:1), yellow solid, 38 mg, yield 48%; m.p. 197-199°C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.18 (s, 1H), 7.99 (d, *J* = 9.2 Hz, 1H), 7.66 (d, *J* = 8.8 Hz, 1H), 3.64 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 153.23 (s), 137.07 (s), 135.52 (s), 134.22 (s), 133.55 (s), 132.75 (s), 118.07 (s), 116.62 (s), 115.14 (s), 30.25 (s). IR (cm^{-1}): 768, 975, 1110, 1195, 1226, 1429, 1540, 1609, 1671, 1716, 2235, 2952. HRMS: $C_{10}H_7BrN_3O$ $[M+H]^+$; found: 263.9767, calculated: 263.9780.



methyl 3-cyano-1-methyl-2-oxo-1,2-dihydroquinoxaline-6-carboxylate (3bf)

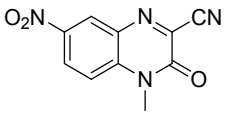
Purified by column chromatography (petroleum ether/ethyl acetate = 10:1), light yellow solid, 57 mg, yield 78%; m.p. 200-203 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.34 (d, *J* = 1.6 Hz, 1H), 8.28 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.79 (d, *J* = 8.8 Hz, 1H), 3.92 (s, 3H), 3.67 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 165.31 (s), 153.37 (s), 137.94 (s), 135.68 (s), 134.21 (s), 132.04 (d, *J* = 6.6 Hz), 125.90 (s), 116.66 (s), 115.06 (s), 53.05 (s), 30.34 (s). IR (cm^{-1}): 768, 1109, 1198, 1226, 1300, 1437, 1541, 1609, 1671, 1717, 2236, 2957, 3090. HRMS: $C_{12}H_{10}N_3O_3$ $[M+H]^+$; found: 244.0713, calculated:

244.0717.



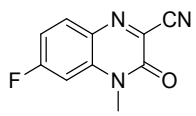
7-benzoyl-4-methyl-3-oxo-3,4-dihydroquinoxaline-2-carbonitrile (3bg)

Purified by column chromatography (petroleum ether/ethyl acetate = 12:1), light yellow solid, 61 mg, yield 70%; m.p. 200-203 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.20 – 8.14 (m, 2H), 7.86 (d, *J* = 8.8 Hz, 1H), 7.79 (d, *J* = 7.2 Hz, 2H), 7.74 (t, *J* = 7.6 Hz, 1H), 7.61 (t, *J* = 7.6 Hz, 2H), 3.71 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 194.15 (s), 153.46 (s), 137.62 (s), 137.00 (s), 135.63 (s), 134.92 (s), 133.49 (s), 133.11 (s), 132.74 (s), 131.84 (s), 130.08 (s), 129.22 (s), 116.60 (s), 115.11 (s), 30.38 (s). IR (cm^{-1}): 643, 724, 1088, 1200, 1233, 1276, 1445, 1541, 1599, 1663, 2243, 2920, 3087. HRMS: $C_{17}H_{12}N_3O_2$ $[M+H]^+$; found: 290.0925, calculated: 290.0924.



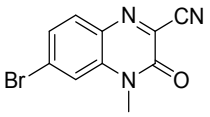
4-methyl-7-nitro-3-oxo-3,4-dihydroquinoxaline-2-carbonitrile (3bh)

Purified by column chromatography (petroleum ether/ethyl acetate = 12:1), light yellow solid, 30 mg, yield 43%; m.p. 256-258 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.73 (d, *J* = 2.4 Hz, 1H), 8.58 (dd, *J* = 9.2, 2.8 Hz, 1H), 7.90 (d, *J* = 9.2 Hz, 1H), 3.70 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 153.35 (s), 143.68 (s), 139.26 (s), 137.16 (s), 131.58 (s), 128.32 (s), 126.27 (s), 117.35 (s), 114.85 (s), 30.64 (s). IR (cm^{-1}): 496, 733, 842, 1078, 1200, 1345, 1460, 1518, 1608, 1675, 2236, 3080, 3110. $C_{10}H_7N_4O_3$ $[M+H]^+$; found: 231.0517, calculated: 231.0513.



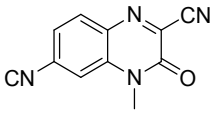
6-fluoro-4-methyl-3-oxo-3,4-dihydroquinoxaline-2-carbonitrile (3bi)

Purified by column chromatography (petroleum ether/ethyl acetate = 10:1), yellow solid, 32 mg, yield 53%; m.p. 228-230 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.01 (dd, *J* = 9.2, 6.0 Hz, 1H), 7.63 (dd, *J* = 10.8, 2.4 Hz, 1H), 7.38 (td, *J* = 8.8, 2.8 Hz, 1H), 3.62 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 165.64 (d, *J* = 253.4 Hz), 153.34 (s), 136.91 (d, *J* = 13.2 Hz), 133.91 (d, *J* = 11.5 Hz), 133.01 (d, *J* = 4.1 Hz), 129.98 (d, *J* = 1.5 Hz), 115.28 (s), 113.34 (d, *J* = 24.4 Hz), 102.92 (d, *J* = 28.6 Hz), 30.47 (s); ^{19}F NMR (376 MHz, DMSO-d_6) δ -101.32 (s). IR (cm^{-1}): 445, 465, 779, 839, 870, 1085, 1250, 1302, 1361, 1453, 1533, 1610, 1664, 2238, 3087. $C_{10}H_7FN_3O$ $[M+H]^+$; found: 204.0563, calculated: 204.0568.



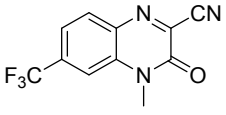
6-bromo-4-methyl-3-oxo-3,4-dihydroquinoxaline-2-carbonitrile (3bj)

Purified by column chromatography (petroleum ether/ethyl acetate = 8:1), yellow solid, 45 mg, yield 57%; m.p. 223-225 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.06 (dd, *J* = 4.8, 2.4 Hz, 1H), 7.89 (dt, *J* = 9.2, 2.8 Hz, 1H), 7.73 (dd, *J* = 9.2, 2.0 Hz, 1H), 3.65 (s, 3H); ^{13}C NMR (151 MHz, DMSO-d_6) δ 153.20 (s), 135.62 (s), 134.40 (s), 133.85 (s), 133.19 (s), 129.74 (s), 128.93 (s), 117.86 (s), 115.13 (s), 30.29 (s). IR (cm^{-1}): 592, 833, 1099, 1197, 1427, 1534, 1667, 2238, 3069. HRMS: $C_{10}H_7BrN_3O$ $[M+H]^+$; found: 263.9767, calculated: 263.9767.



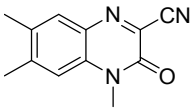
6-isocyano-4-methyl-3-oxo-3,4-dihydroquinoxaline-2-carbonitrile (3bk)

Purified by column chromatography (petroleum ether/ethyl acetate = 10:1), yellow solid, 39 mg, yield 62%; m.p. 248-250 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.55 (d, *J* = 1.6 Hz, 1H), 8.23 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.85 (d, *J* = 8.8 Hz, 1H), 3.66 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 153.33 (s), 137.96 (s), 136.66 (s), 136.48 (s), 135.69 (s), 132.12 (s), 118.14 (s), 117.55 (s), 114.94 (s), 107.27 (s), 30.35 (s). IR (cm^{-1}): 623, 839, 1086, 1206, 1540, 1609, 1672, 2228, 3058. HRMS: $C_{11}H_7N_4O$ $[M+H]^+$; found: 211.0629, calculated: 211.0624.



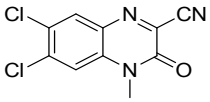
4-methyl-3-oxo-6-(trifluoromethyl)-3,4-dihydroquinoxaline-2-carbonitrile (3bl)

Purified by column chromatography (petroleum ether/ethyl acetate = 8:1), light yellow solid, 39 mg, yield 51%; m.p. 163-165 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 1.2 Hz, 1H), 8.00 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.57 (d, *J* = 8.8 Hz, 1H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.55 (s), 136.19 (s), 135.44 (s), 132.00 (s), 130.68 (q, *J* = 3.3 Hz), 129.19 (q, *J* = 4.0 Hz), 127.37 (q, *J* = 34.0 Hz), 123.10 (q, *J* = 270.5 Hz), 115.31 (s), 113.48 (s), 30.11 (s); ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.40 (s). IR (cm^{-1}): 489, 658, 836, 927, 1096, 1131, 1203, 1228, 1339, 1460, 1543, 1621, 1678, 2231, 3073. HRMS: $C_{11}H_7F_3N_3O$ $[M+H]^+$; found: 254.0548, calculated: 254.0536.



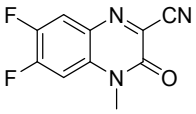
4,6,7-trimethyl-3-oxo-3,4-dihydroquinoxaline-2-carbonitrile (3bm)

Purified by column chromatography (petroleum ether/ethyl acetate = 10:1), light yellow solid, 50 mg, yield 78%; m.p. 237-239 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.68 (s, 1H), 7.52 (s, 1H), 3.63 (s, 3H), 2.45 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 158.27 (s), 150.88 (s), 139.01 (s), 137.77 (s), 136.88 (s), 136.25 (s), 135.31 (s), 120.81 (s), 120.44 (s), 34.76 (s), 25.63 (s), 23.74 (s). IR (cm^{-1}): 431, 1189, 1256, 1458, 1519, 1618, 1651, 2233, 2996. HRMS: $C_{12}H_{12}N_3O$ $[M+H]^+$; found: 214.0979, calculated: 214.0975.



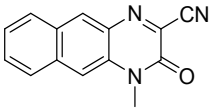
6,7-dichloro-4-methyl-3-oxo-3,4-dihydroquinoxaline-2-carbonitrile (3bn)

Purified by column chromatography (petroleum ether/ethyl acetate = 10:1), light yellow solid, 49 mg, yield 65%; m.p. 272-274 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.30 (s, 1H), 8.06 (s, 1H), 3.64 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 153.10 (s), 137.31 (s), 135.76 (s), 134.62 (s), 131.99 (s), 131.58 (s), 127.20 (s), 117.83 (s), 115.03 (s), 30.49 (s). IR (cm^{-1}): 520, 625, 903, 1195, 1448, 1531, 1592, 1658, 2246, 3038, 3089. $C_{10}H_6Cl_2N_3O$ $[M+H]^+$; found: 253.9885, calculated: 253.9882.



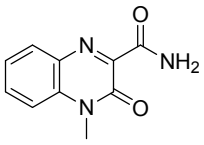
6,7-difluoro-4-methyl-3-oxo-3,4-dihydroquinoxaline-2-carbonitrile (3bo)

Purified by column chromatography (petroleum ether/ethyl acetate = 12:1), light yellow solid, 40 mg, yield 60%; m.p. 183-185 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.77 (m, 1H), 7.24 (dd, *J* = 10.8, 6.8 Hz, 1H), 3.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.39 (dd, *J* = 261.8, 14.6 Hz), 152.42 (s), 147.58 (dd, *J* = 251.6, 14.3 Hz), 134.02 (d, *J* = 4.4 Hz), 132.02 (d, *J* = 7.9 Hz), 129.08 (d, *J* = 12.0 Hz), 119.22 (dd, *J* = 18.2, 2.9 Hz), 113.60 (s), 103.05 (d, *J* = 23.5 Hz), 30.37 (s); ^{19}F NMR (376 MHz, $CDCl_3$) δ -121.42 (d, *J* = 22.1 Hz), -138.49 (d, *J* = 22.1 Hz). IR (cm^{-1}): 655, 786, 896, 1273, 1383, 1460, 1539, 1589, 1667, 2236, 3083. HRMS: $C_{10}H_6F_2N_3O$ $[M+H]^+$; found: 222.0484, calculated: 222.0478.



4-methyl-3-oxo-3,4-dihydrobenzo[g]quinoxaline-2-carbonitrile (3bp)

Purified by column chromatography (petroleum ether/ethyl acetate = 12:1), light yellow solid, 44 mg, yield 62%; m.p. 271-273 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.64 (s, 1H), 8.14 (m, 3H), 7.73 (t, *J* = 7.6 Hz, 1H), 7.59 (t, *J* = 7.6 Hz, 1H), 3.71 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 152.88 (s), 135.76 (s), 135.55 (s), 132.14 (s), 131.71 (s), 131.60 (s), 130.18 (s), 129.73 (s), 129.54 (s), 127.93 (s), 126.44 (s), 115.41 (s), 112.11 (s), 29.91 (s). IR (cm^{-1}): 427, 766, 886, 1148, 1200, 1541, 1593, 1627, 1659, 2227, 3077. HRMS: $C_{14}H_{10}N_3O$ $[M+H]^+$; found: 236.0816, calculated: 236.0818.



4-methyl-3-oxo-3,4-dihydroquinoxaline-2-carboxamide (4)[2]

Purified by column chromatography (petroleum ether/ethyl acetate = 1:1), light yellow solid, 44 mg, yield 72%; m.p. 165-167 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.21 (s, 1H), 7.88 (d, J = 8.0 Hz, 1H), 7.83 (s, 1H), 7.73 (t, J = 7.6 Hz, 1H), 7.63 (d, J = 8.4 Hz, 1H), 7.45 (t, J = 7.6 Hz, 1H), 3.67 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 165.61 (s), 153.30 (s), 152.06 (s), 134.07 (s), 132.26 (s), 131.90 (s), 130.36 (s), 124.40 (s), 115.47 (s), 29.53 (s). HRMS: $C_{10}H_{10}N_3O_2$ $[M+H]^+$; found: 204.0762, calculated: 204.0766.

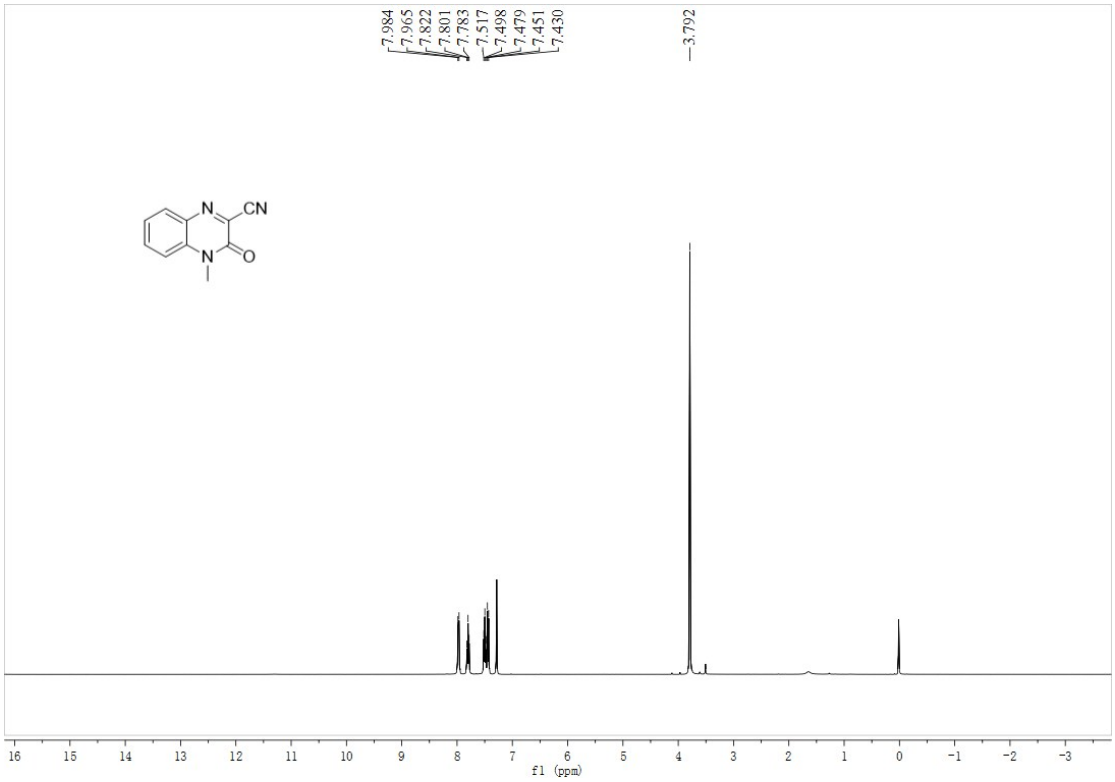
5. References

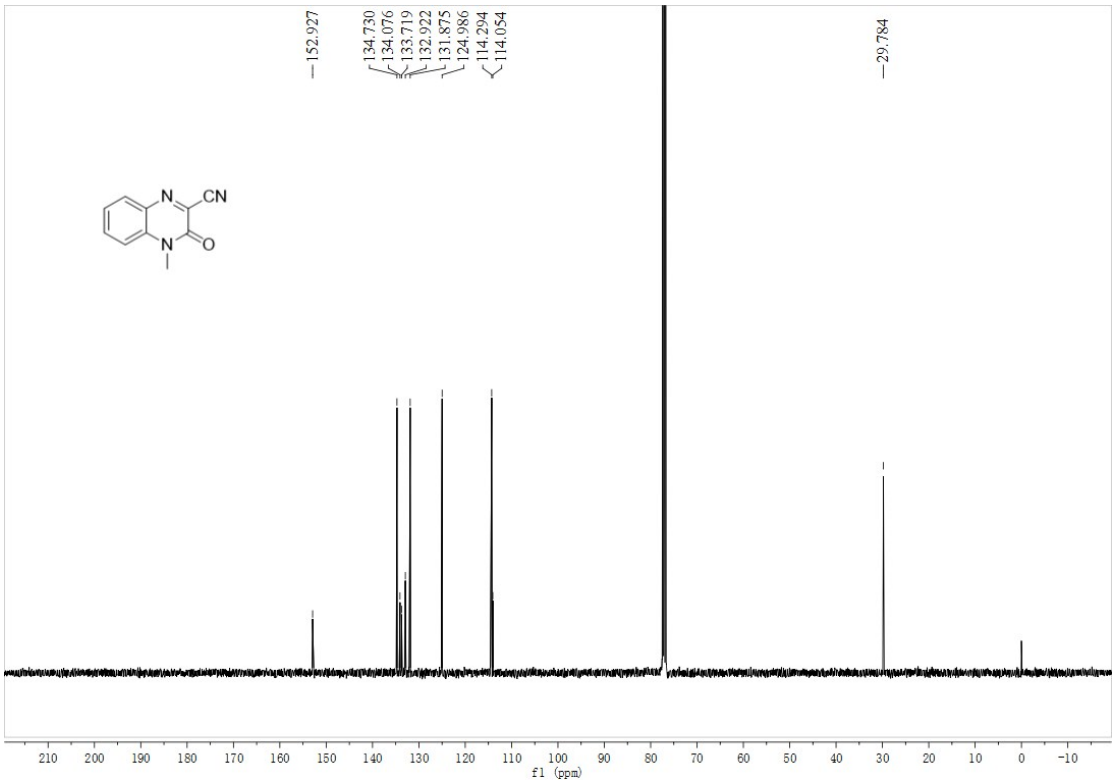
1 A. Carrër, J. D. Brion, S. Messaoudi and M. Alami, *Org. Lett*., 2013, **15**, 5607.

2 F. Wang, B.-L. Hu, L. Liu, H.-Y. Tu and X.-G. Zhang, *J. Org. Chem*., 2017, **82**, 11247.

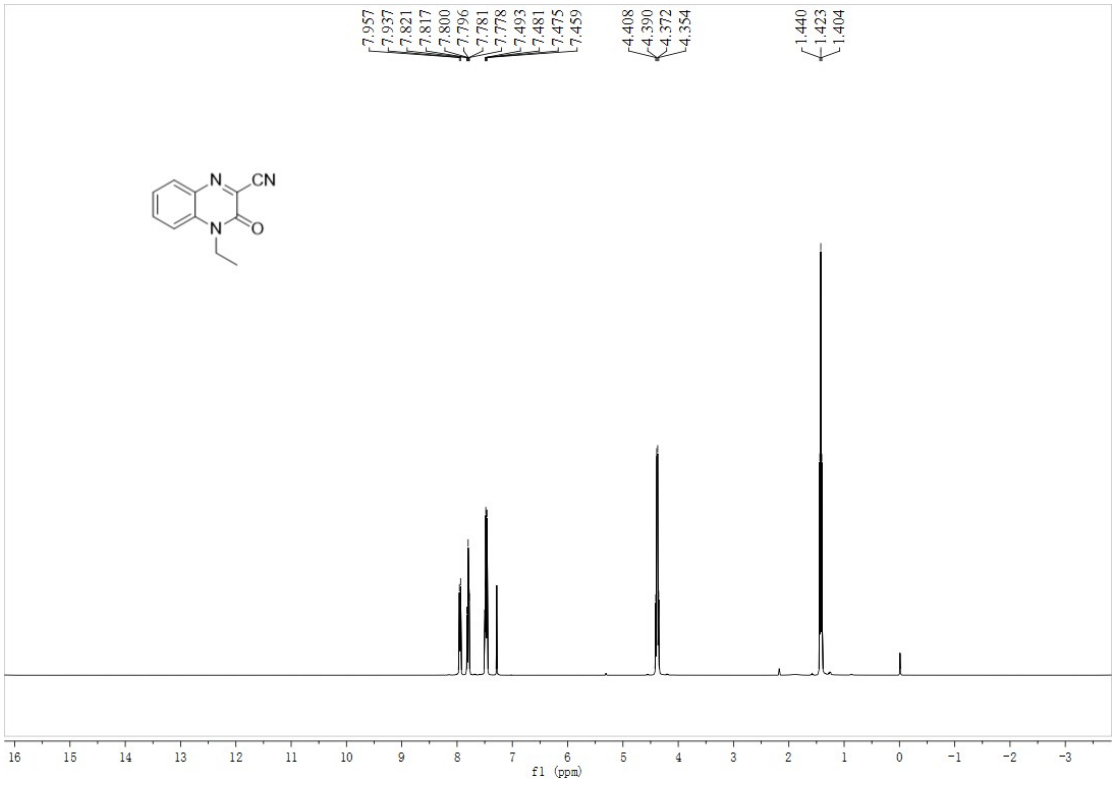
6. ^{1}H, ^{13}C and ^{19}F NMR spectra of the products

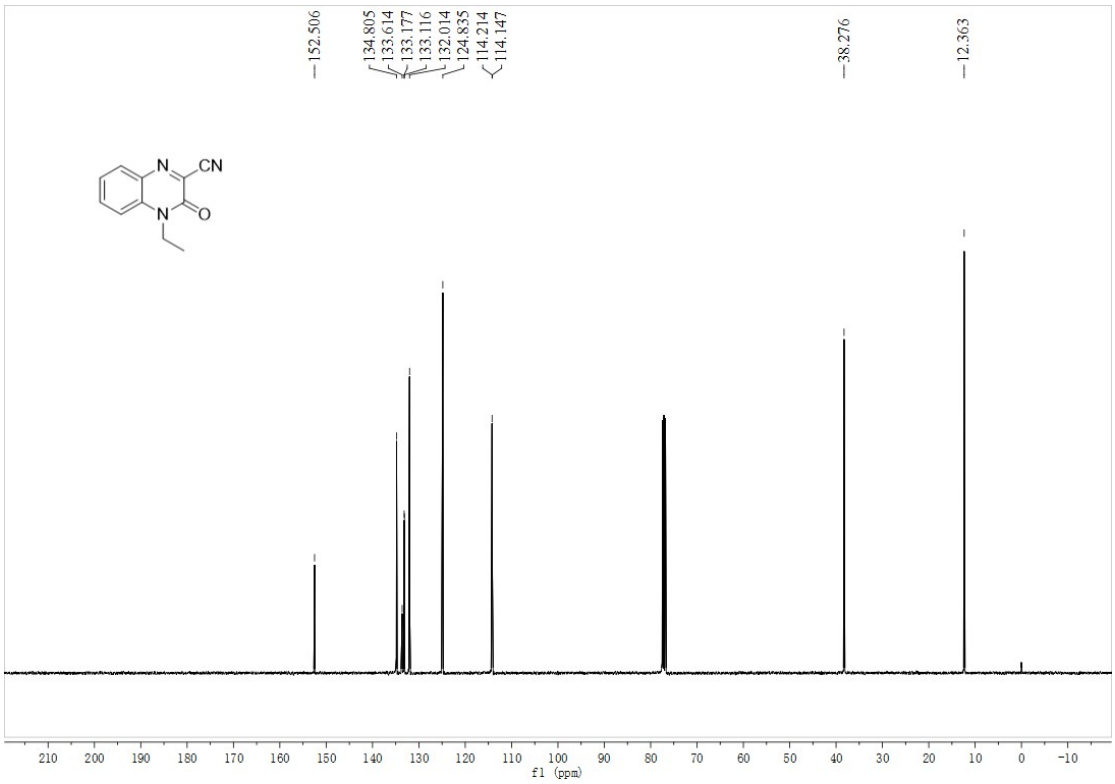
4-methyl-3-oxo-3,4-dihydroquinoxaline-2-carbonitrile (3aa)



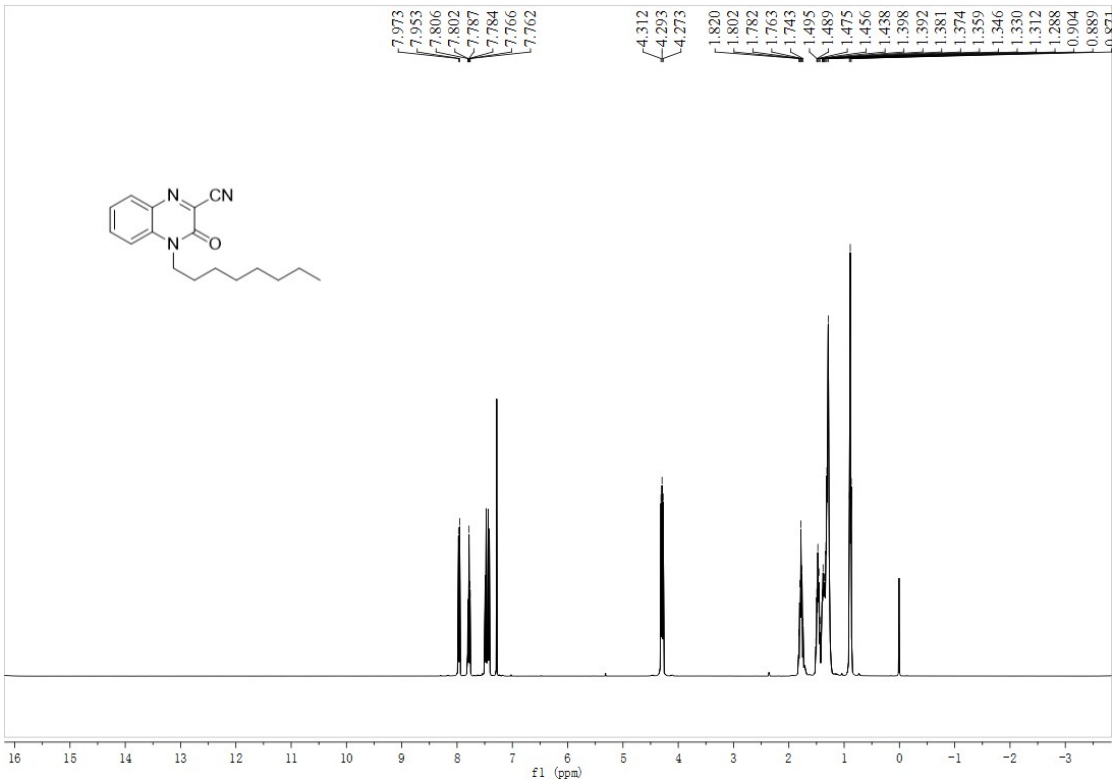


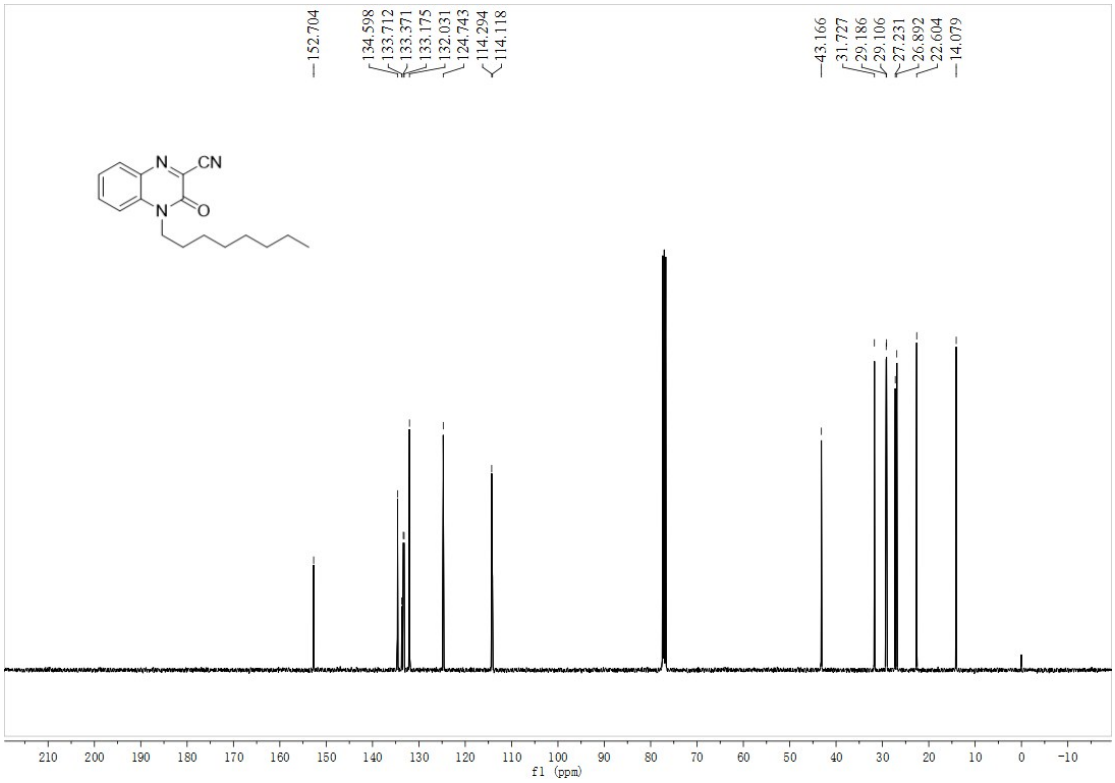
4-ethyl-3-oxo-3,4-dihydroquinoxaline-2-carbonitrile (3ab)



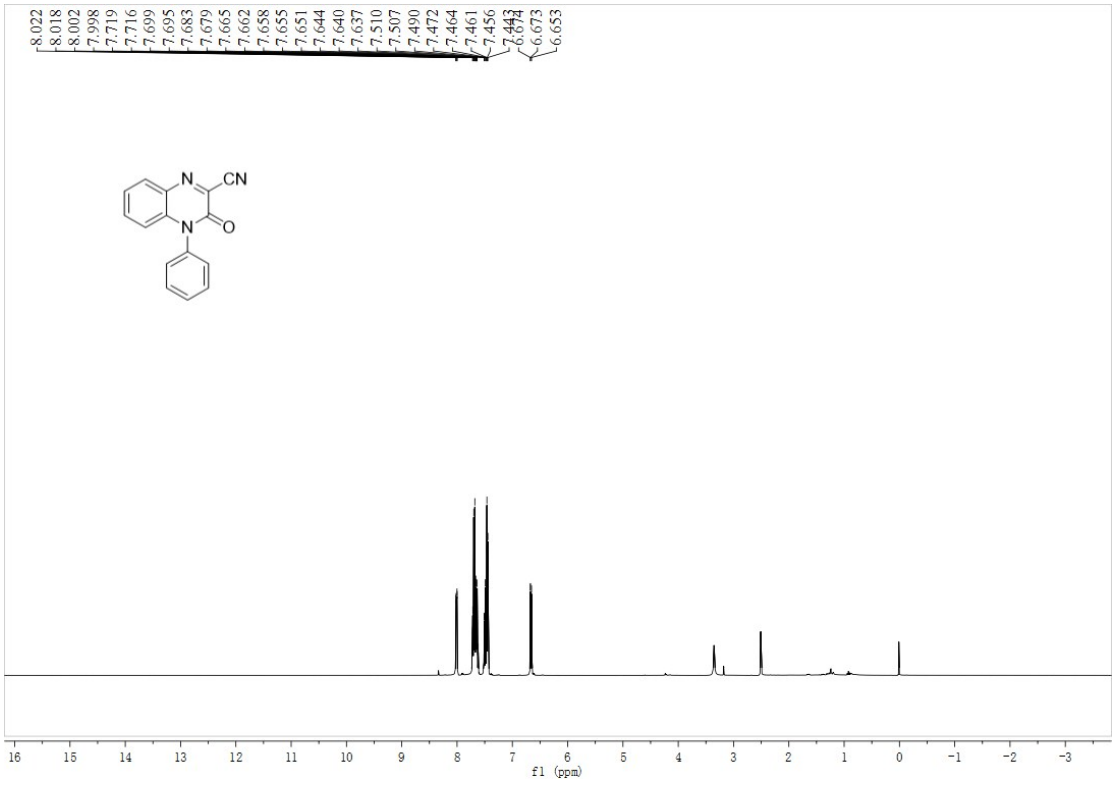


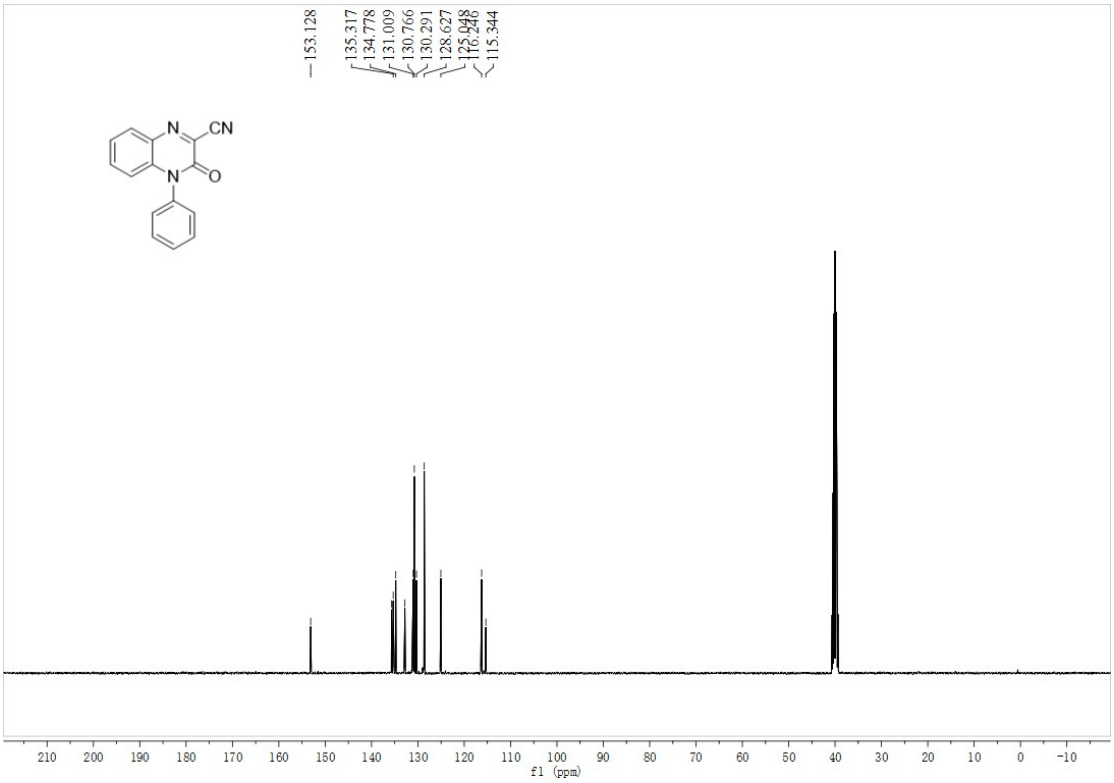
4-octyl-3-oxo-3,4-dihydroquinoxaline-2-carbonitrile (3ac)


7.973
7.953
7.806
7.802
7.787
7.784
7.766
7.762
4.312
4.293
4.273
1.820
1.802
1.782
1.763
1.743
1.495
1.489
1.475
1.456
1.438
1.398
1.392
1.381
1.374
1.359
1.346
1.330
1.312
1.288
0.904
0.889
N
CN
N
O
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

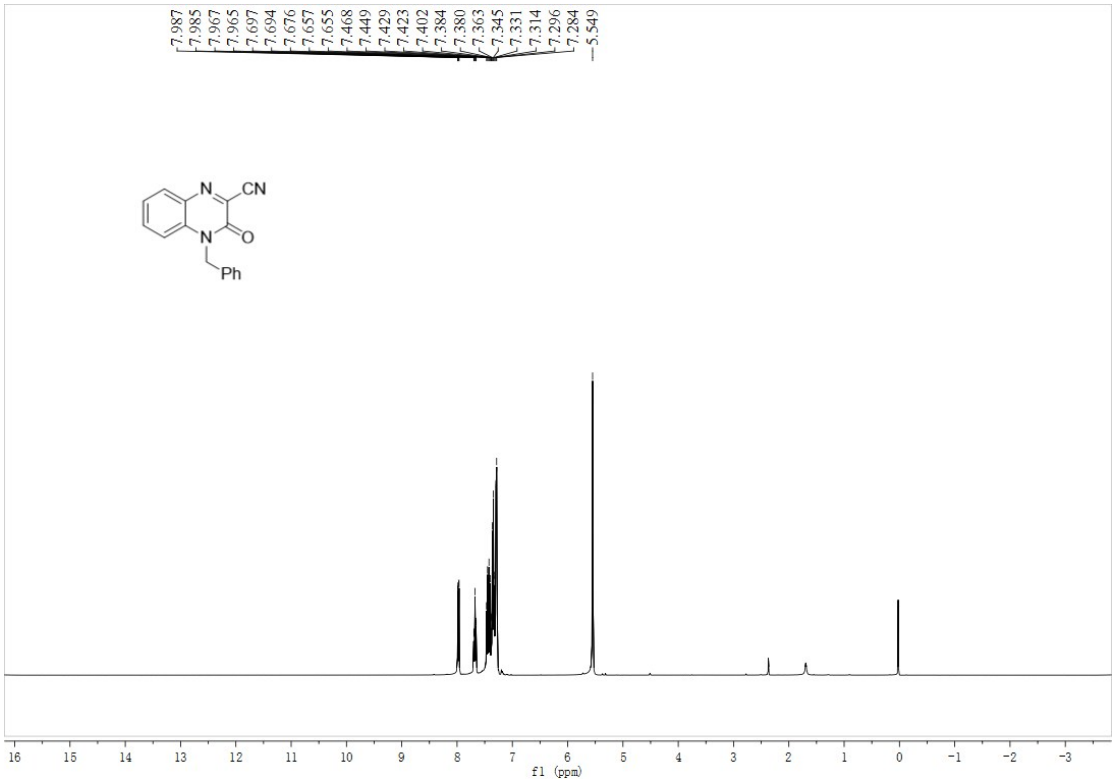

152.704
134.598
133.712
133.371
133.175
132.031
124.743
114.294
114.118
43.166
31.727
29.186
29.106
27.231
26.892
22.604
14.079
N
CN
N
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

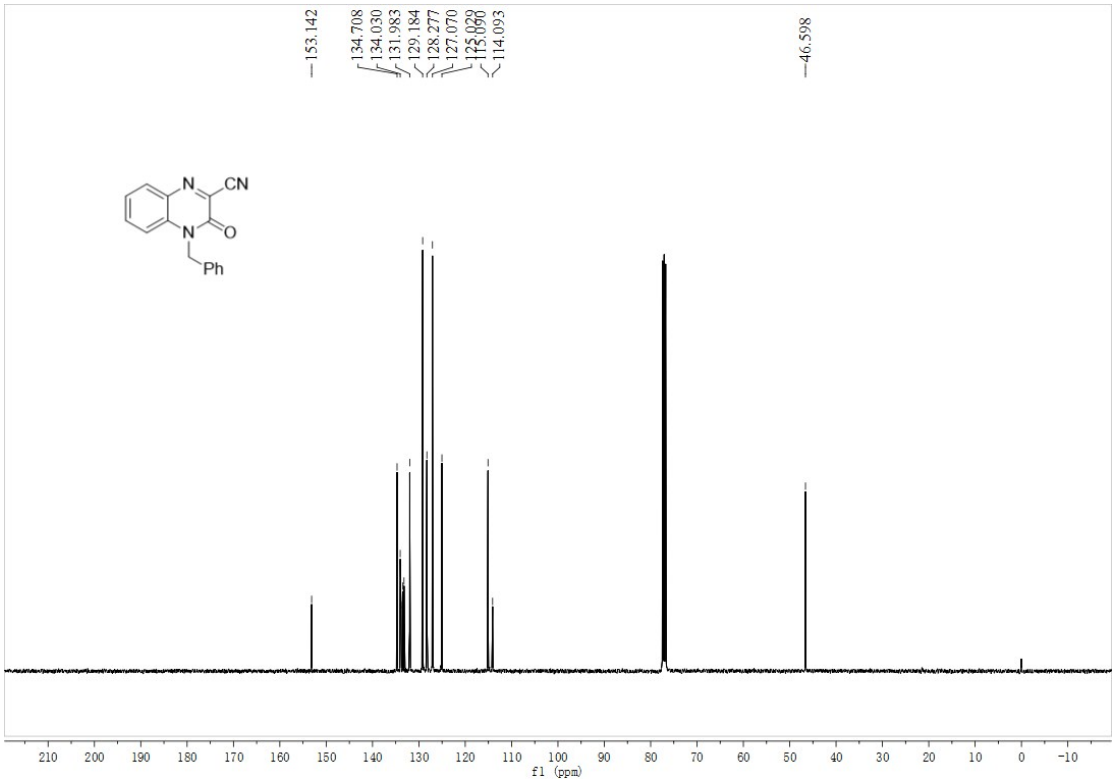
3-oxo-4-phenyl-3,4-dihydroquinoxaline-2-carbonitrile (3ad)



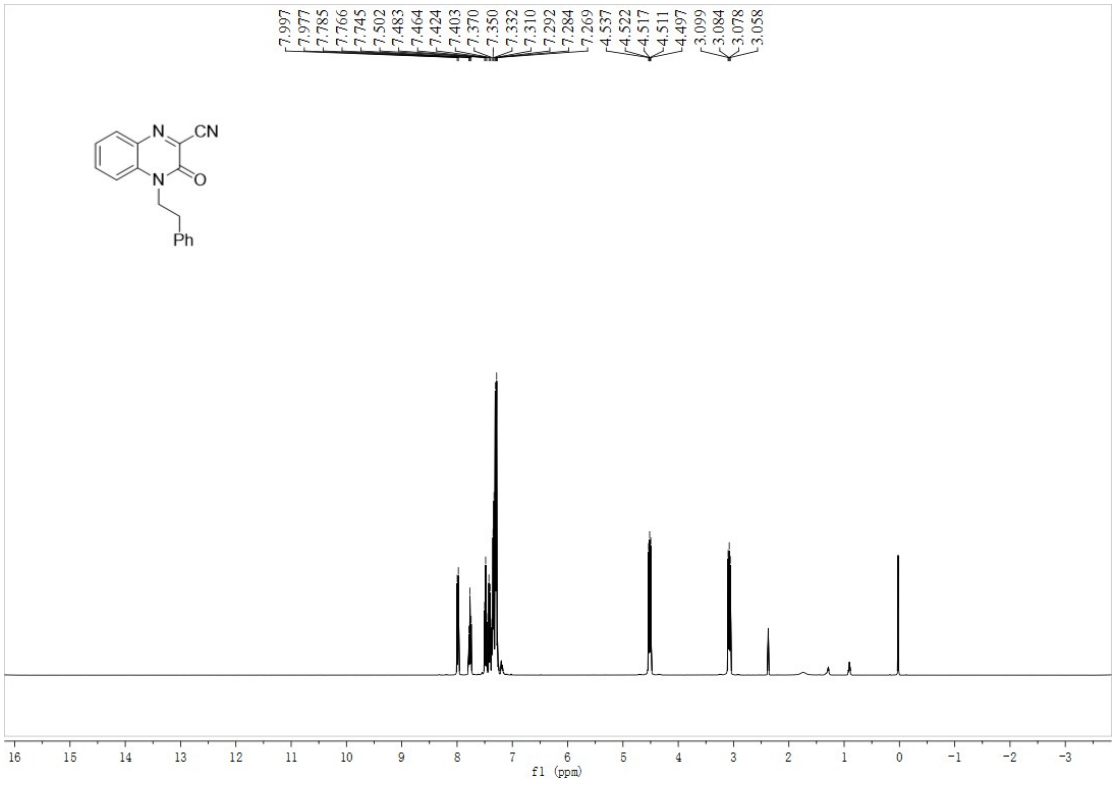


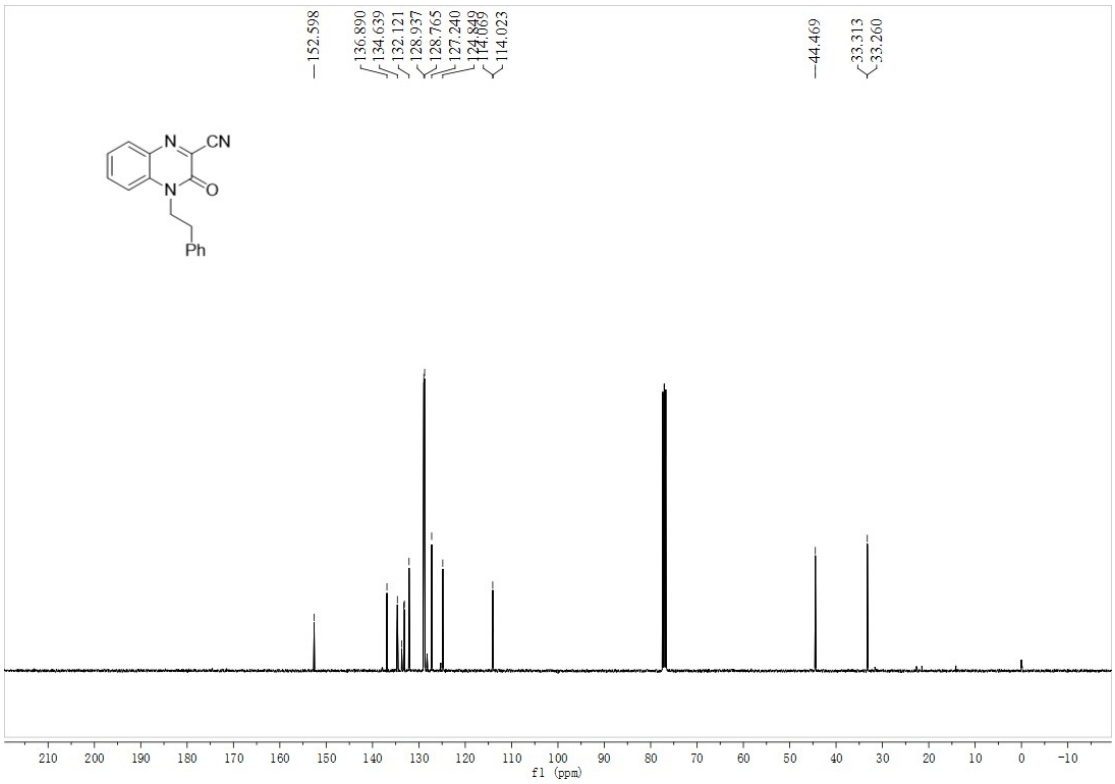
4-benzyl-3-oxo-3,4-dihydroquinoxaline-2-carbonitrile (3ae)


7.987
7.985
7.967
7.965
7.697
7.694
7.676
7.657
7.655
7.468
7.449
7.429
7.423
7.402
7.384
7.380
7.363
7.345
7.331
7.314
7.296
7.284
5.549
N
CN
N
O
Ph
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

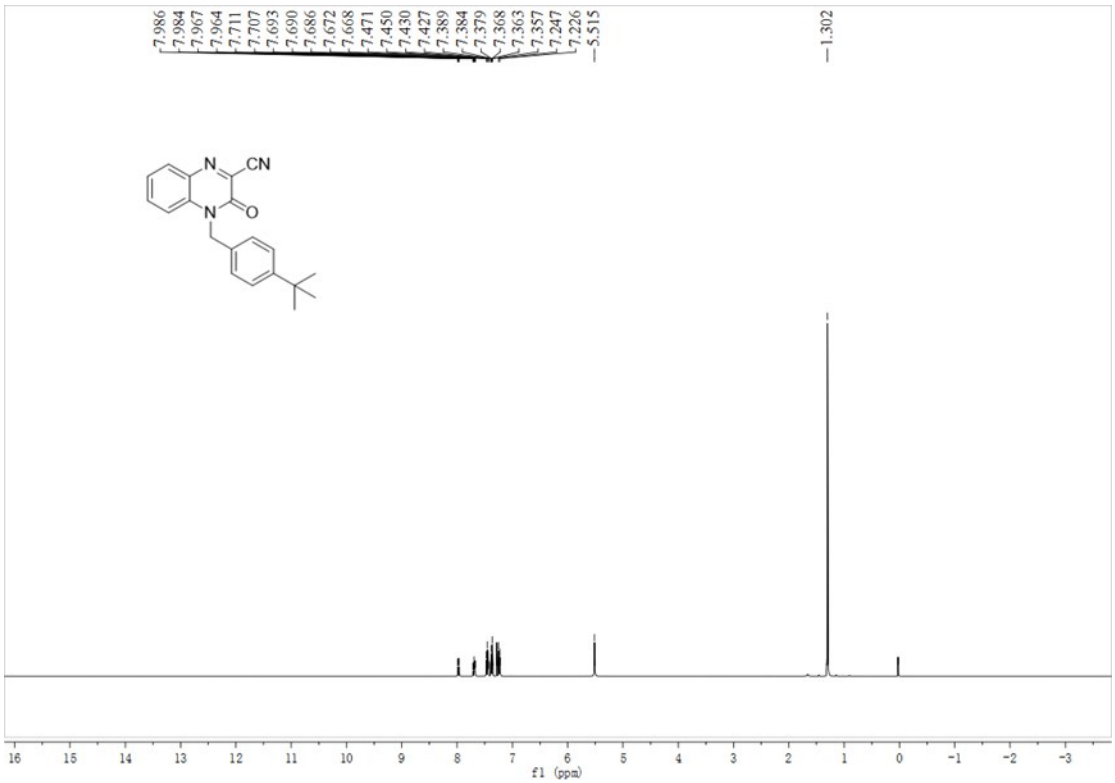

153.142
134.708
134.030
131.983
129.184
128.277
127.070
125.029
115.090
114.093
46.598
N
CN
N
O
Ph
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

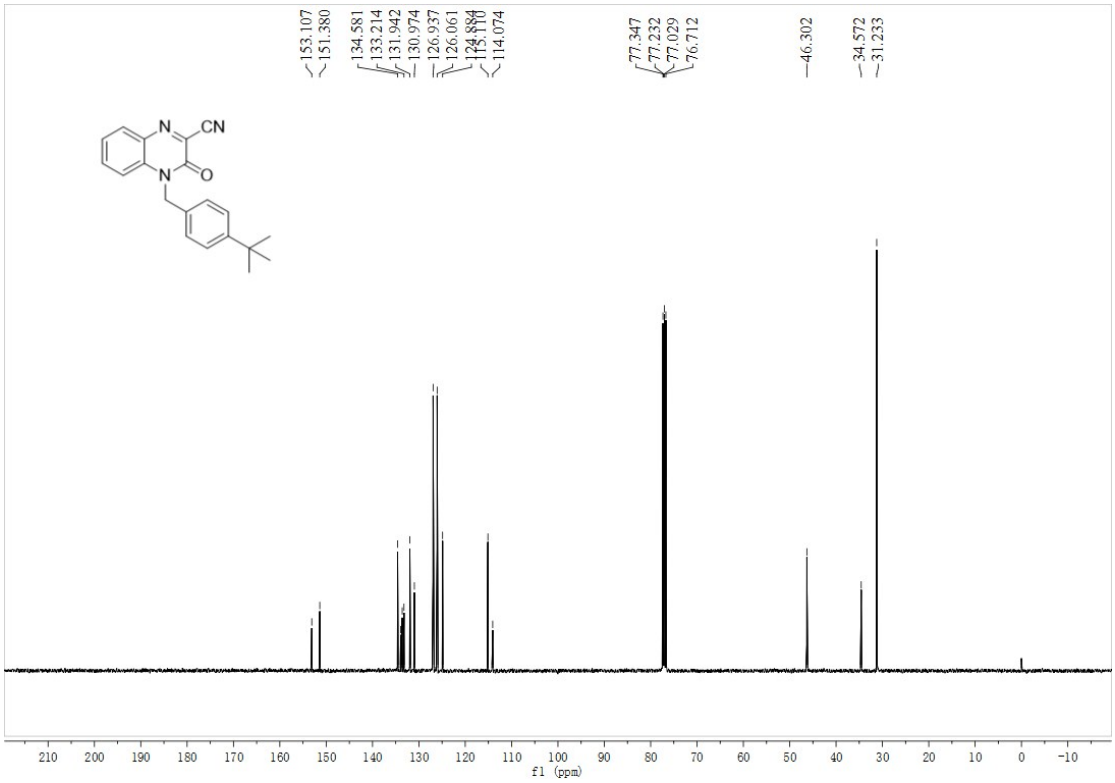
3-oxo-4-phenethyl-3,4-dihydroquinoxaline-2-carbonitrile (3af)



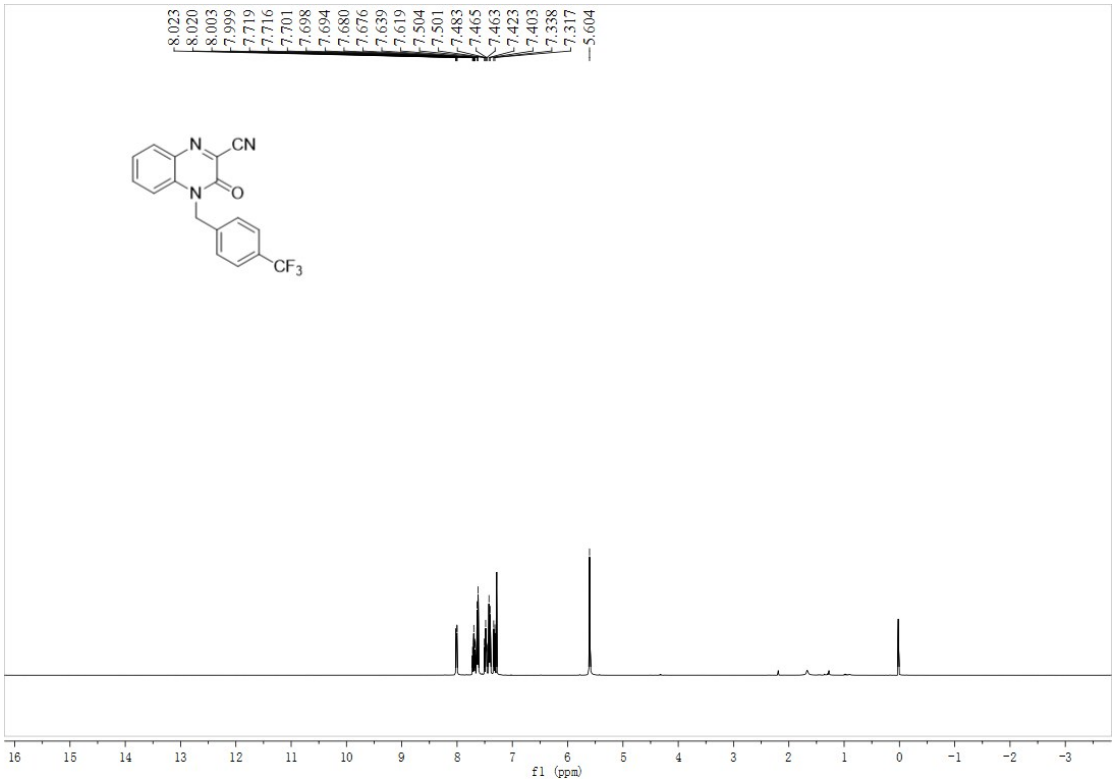


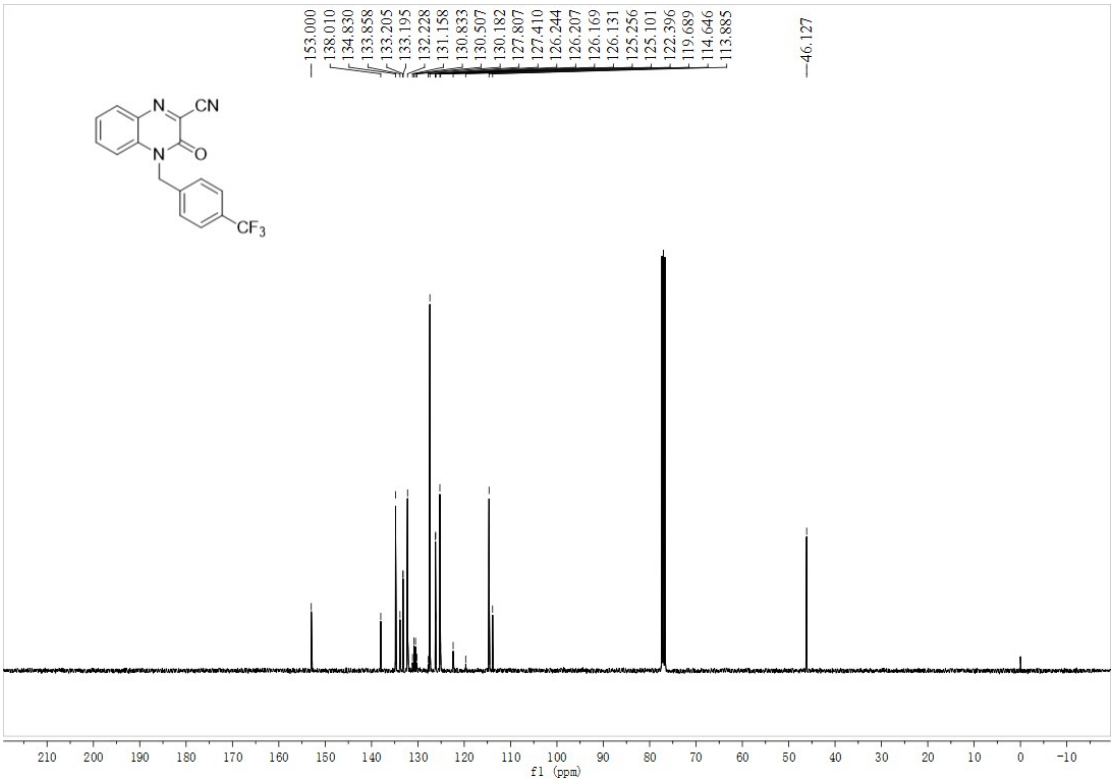
4-(4-(*tert*-butyl)benzyl)-3-oxo-3,4-dihydroquinoxaline-2-carbonitrile (3ag)

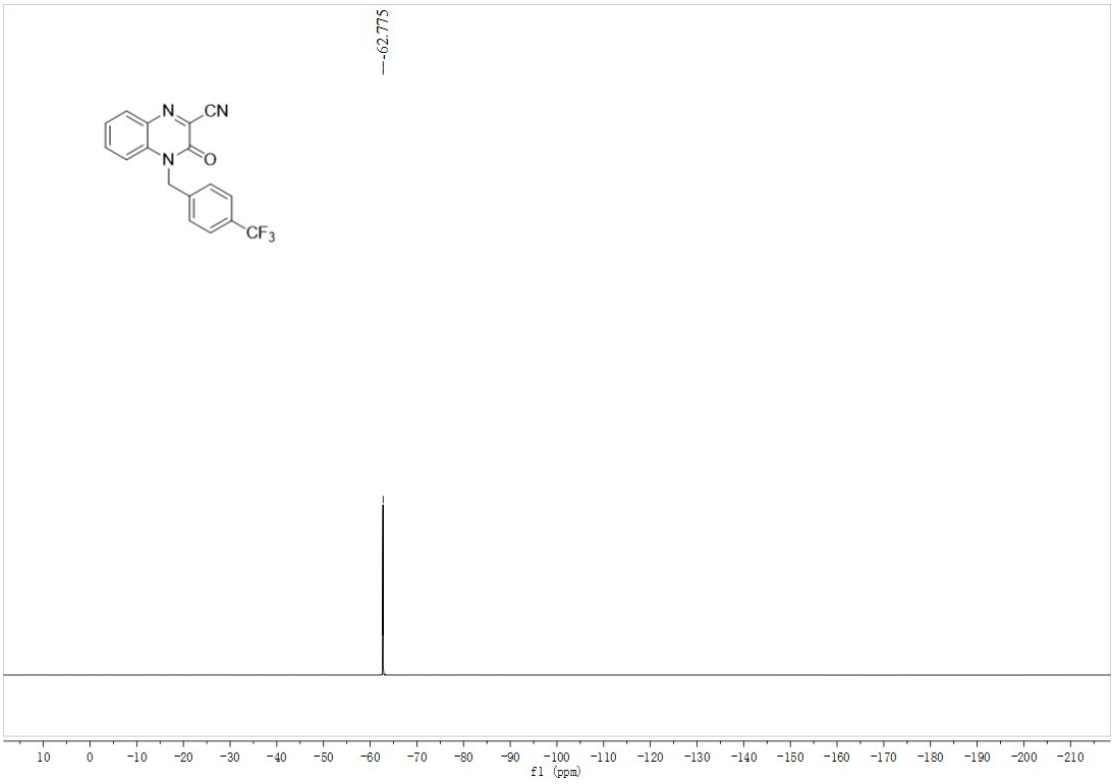

7.986
7.984
7.967
7.964
7.711
7.707
7.693
7.690
7.686
7.672
7.668
7.471
7.450
7.430
7.427
7.389
7.384
7.379
7.368
7.363
7.357
7.247
7.226
5.515
1.302
N
CN
N
O
f1 (ppm)


153.107
151.380
134.581
133.214
131.942
130.974
126.937
126.061
124.884
115.110
114.074
77.347
77.232
77.029
76.712
46.302
34.572
31.233
N
CN
N
O
f1 (ppm)

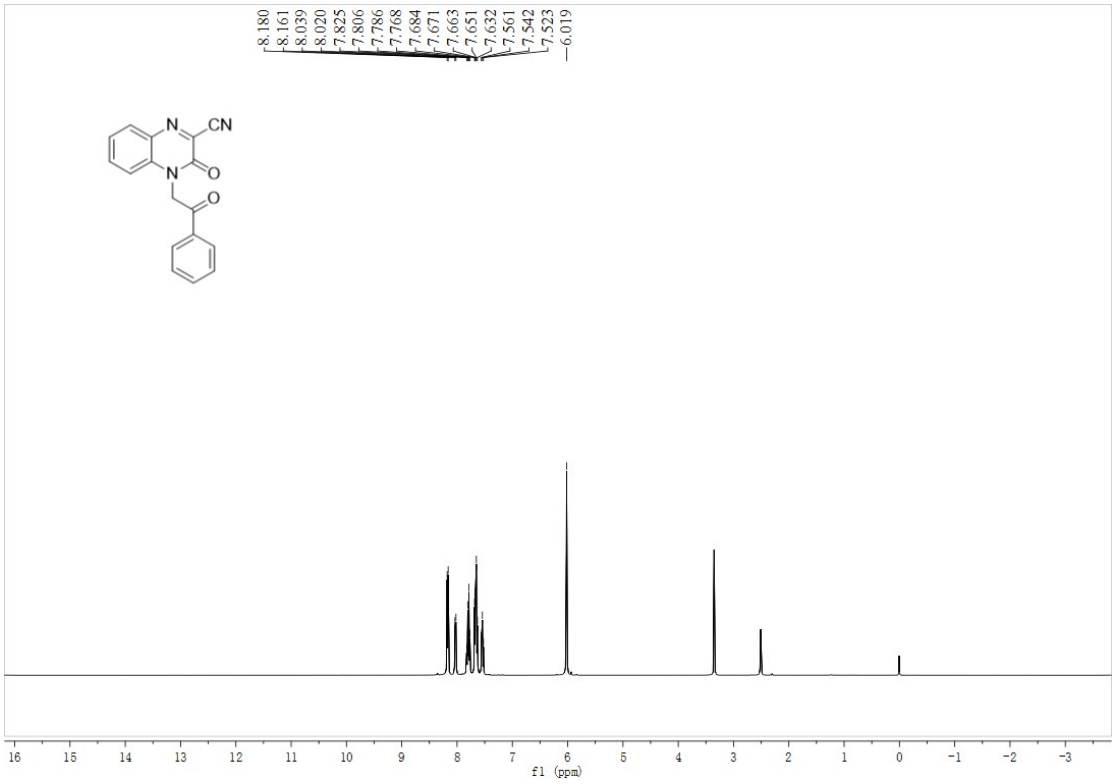
3-oxo-4-(4-(trifluoromethyl)benzyl)-3,4-dihydroquinoxaline-2-carbonitrile (3ah)

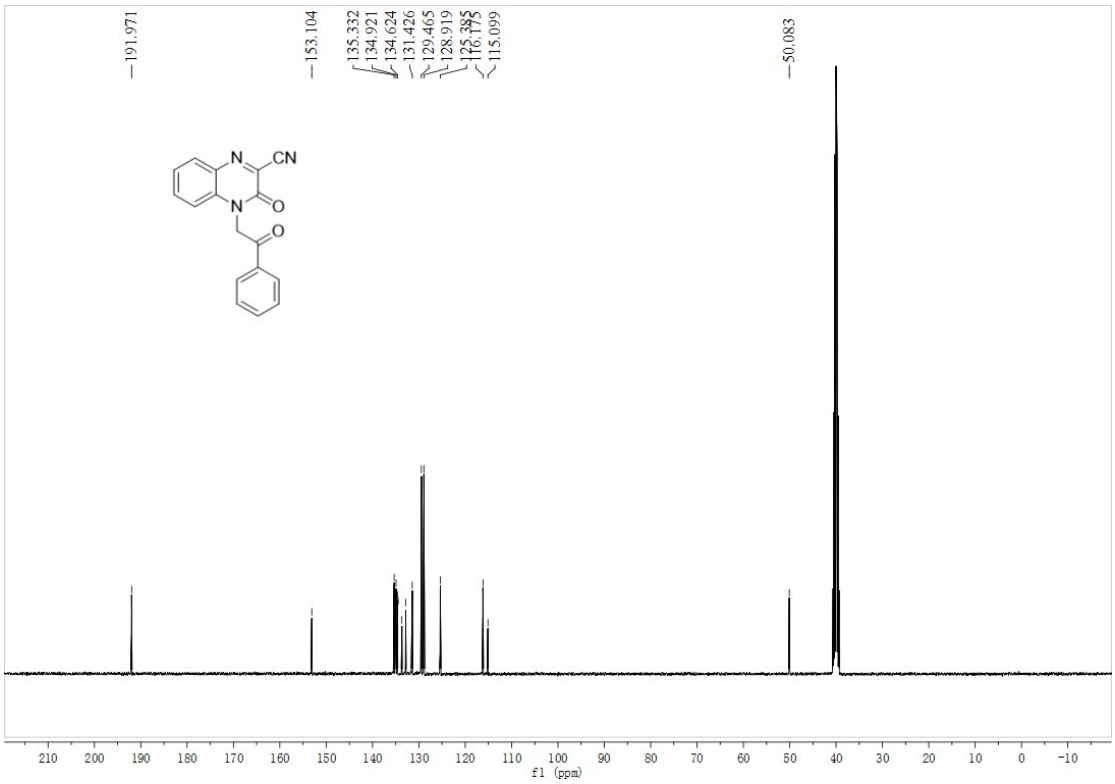



153.000
138.010
134.830
133.858
133.205
133.195
132.228
131.158
130.833
130.507
130.182
127.807
127.410
126.244
126.207
126.169
126.131
125.256
125.101
122.396
119.689
114.646
113.885
46.127
N
CN
O
CF3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

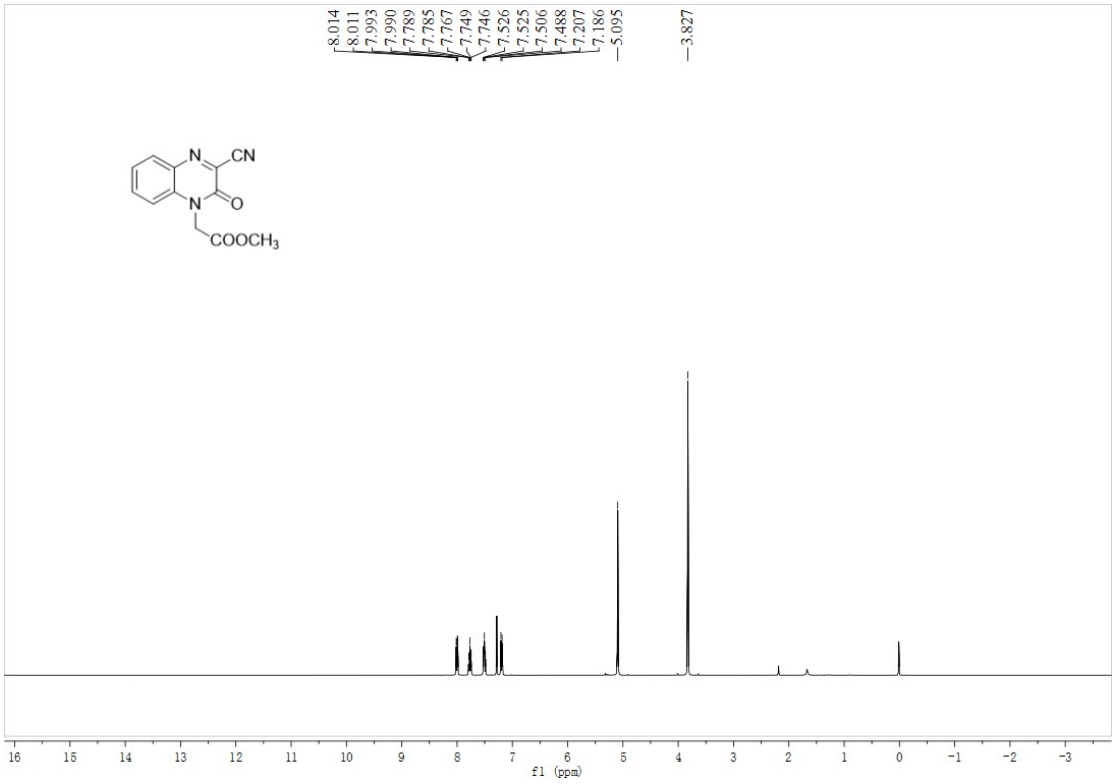

-62.775
N
CN
O
CF3
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

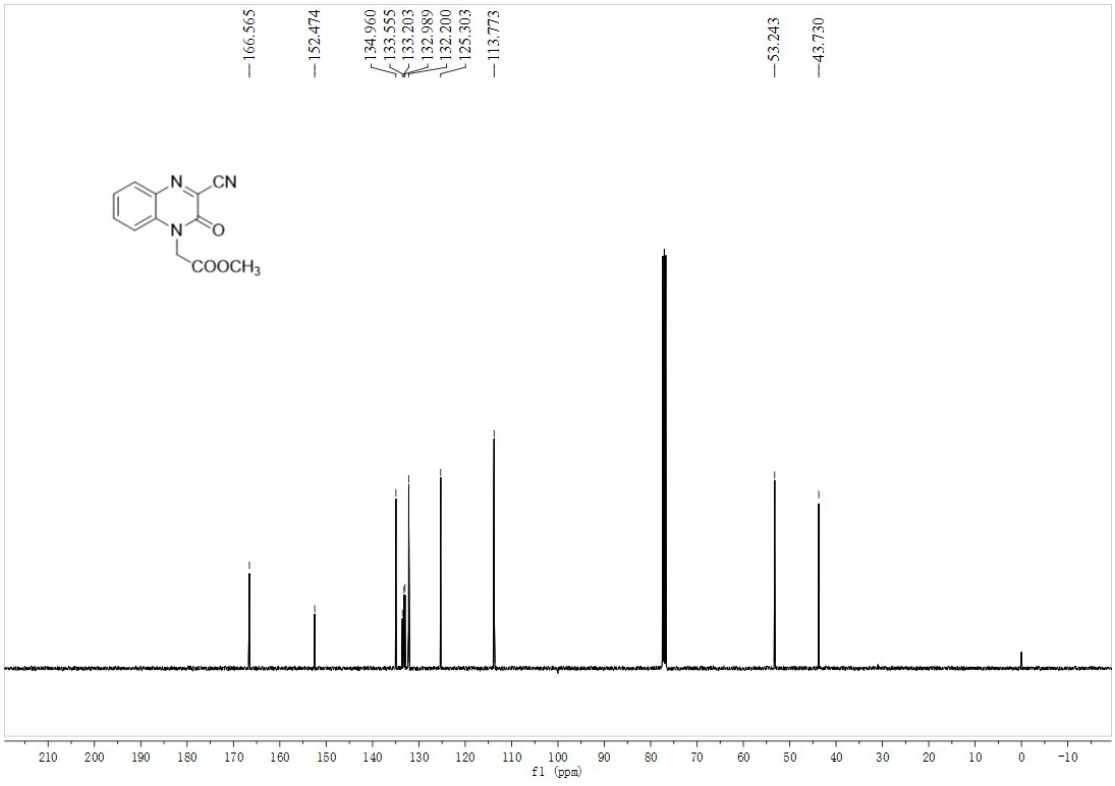
3-oxo-4-(2-oxo-2-phenylethyl)-3,4-dihydroquinoxaline-2-carbonitrile (3ai)



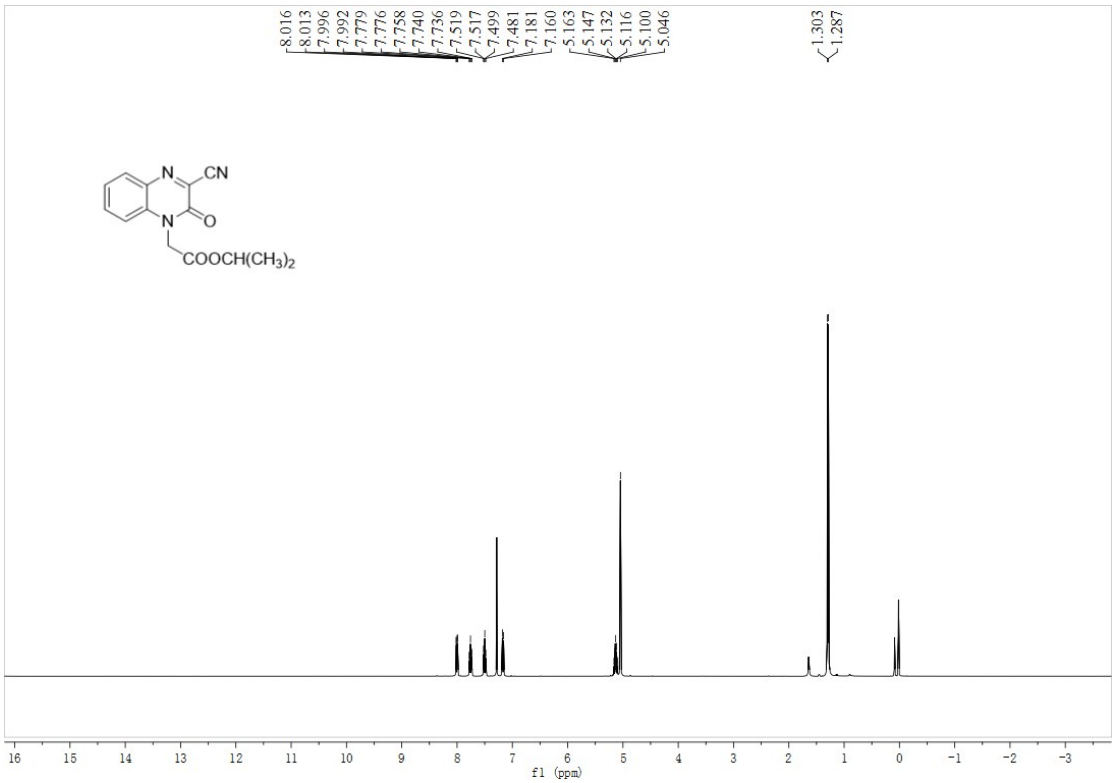


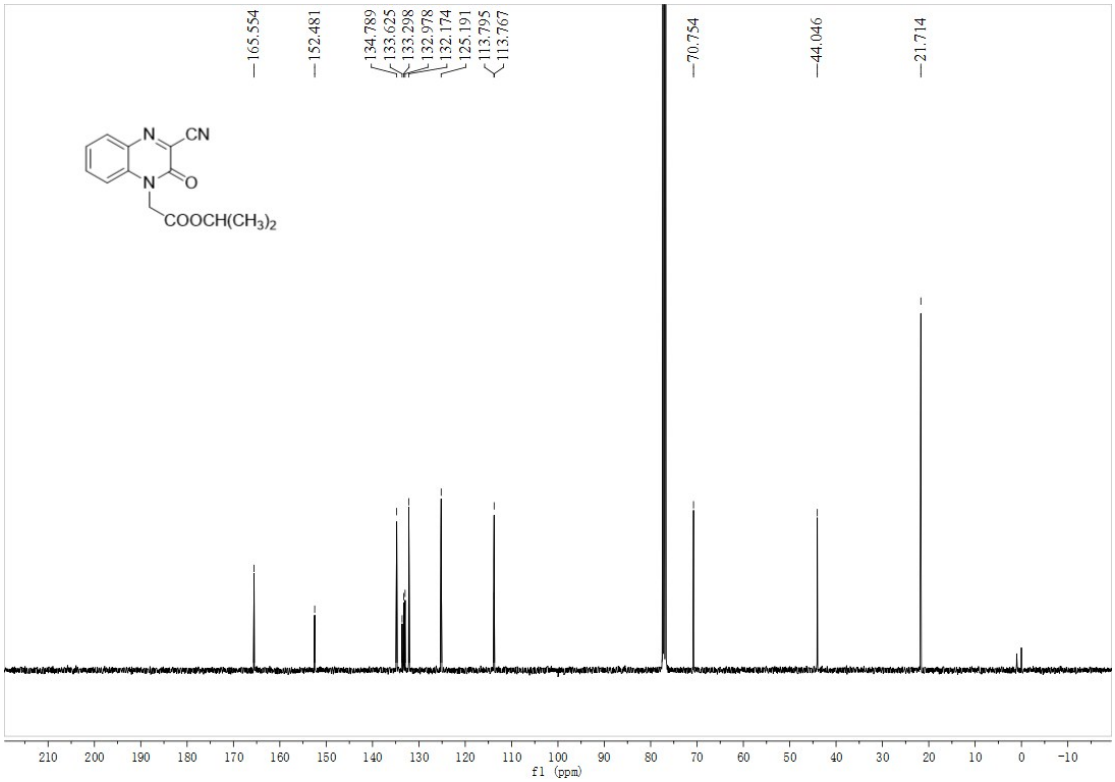
methyl 2-(3-cyano-2-oxoquinoxalin-1(2*H*)-yl)acetate (3aj)



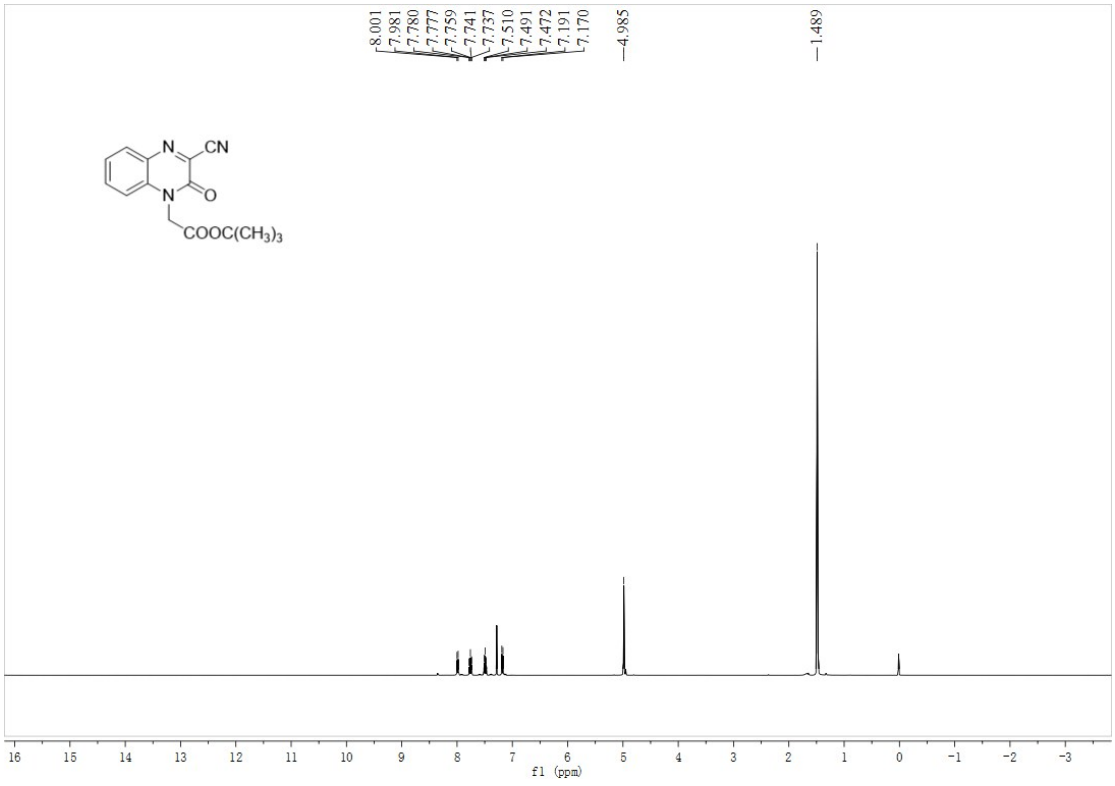


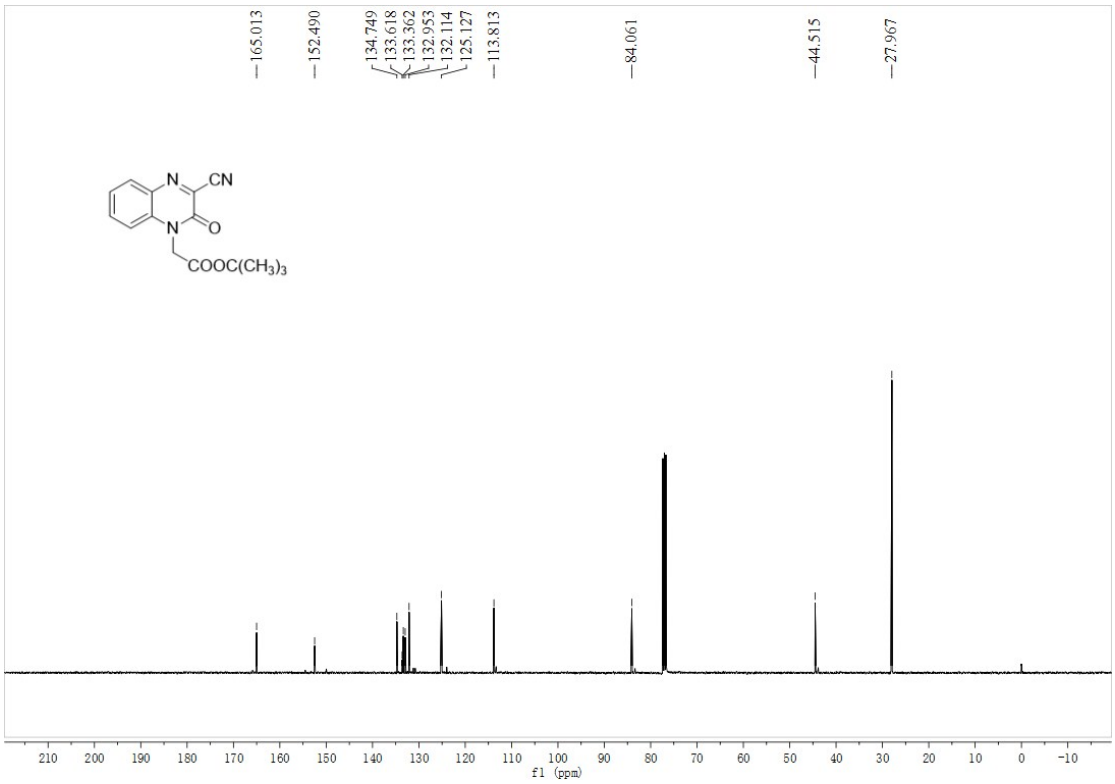
isopropyl 2-(3-cyano-2-oxoquinoxalin-1(2*H*)-yl)acetate (3ak)


8.016
8.013
7.996
7.992
7.779
7.776
7.758
7.740
7.736
7.519
7.517
7.499
7.481
7.181
7.160
5.163
5.147
5.132
5.116
5.100
5.046
1.303
1.287
N
CN
N
O
COOCH(CH3)2
f1 (ppm)

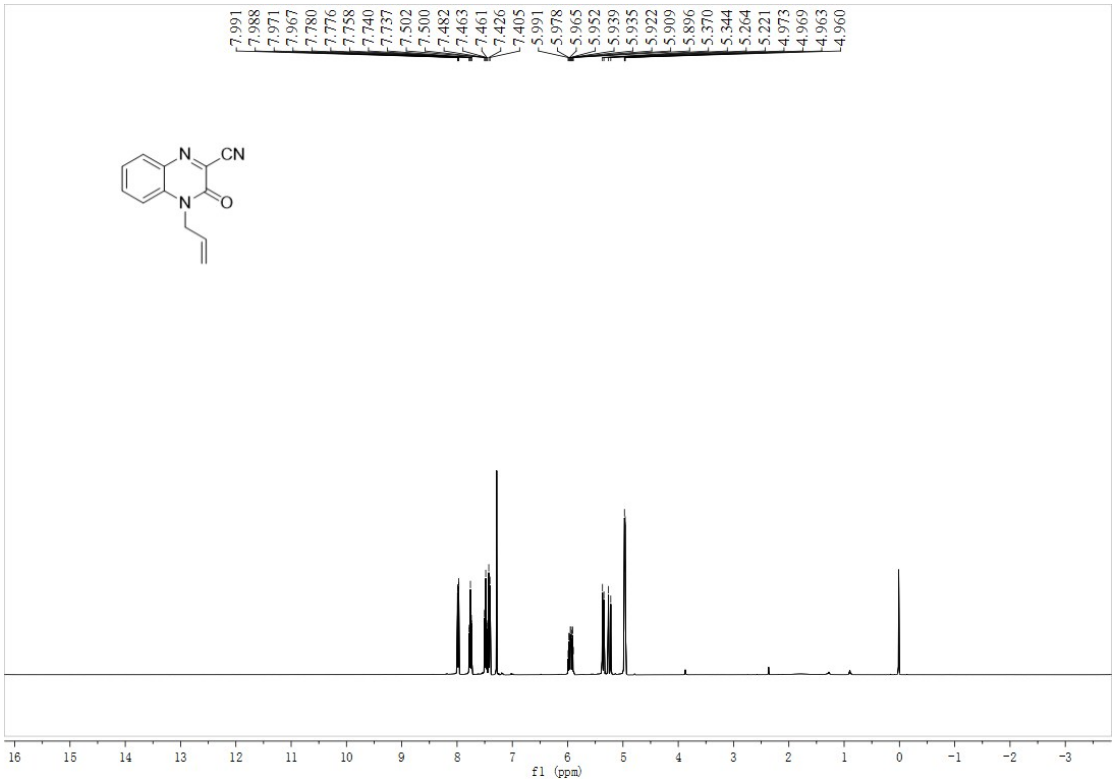

165.554
152.481
134.789
133.625
133.298
132.978
132.174
125.191
113.795
113.767
70.754
44.046
21.714
N
CN
N
O
COOCH(CH3)2
f1 (ppm)

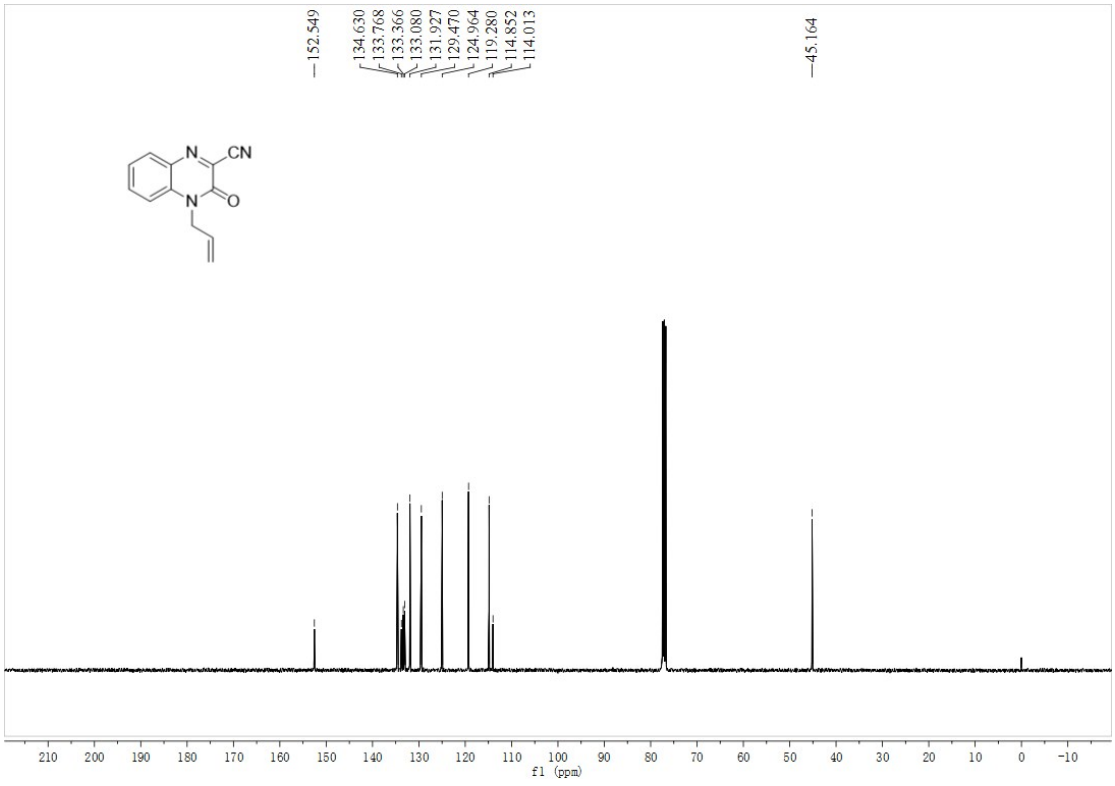
***tert*-butyl 2-(3-cyano-2-oxoquinoxalin-1(2*H*)-yl)acetate (3al)**



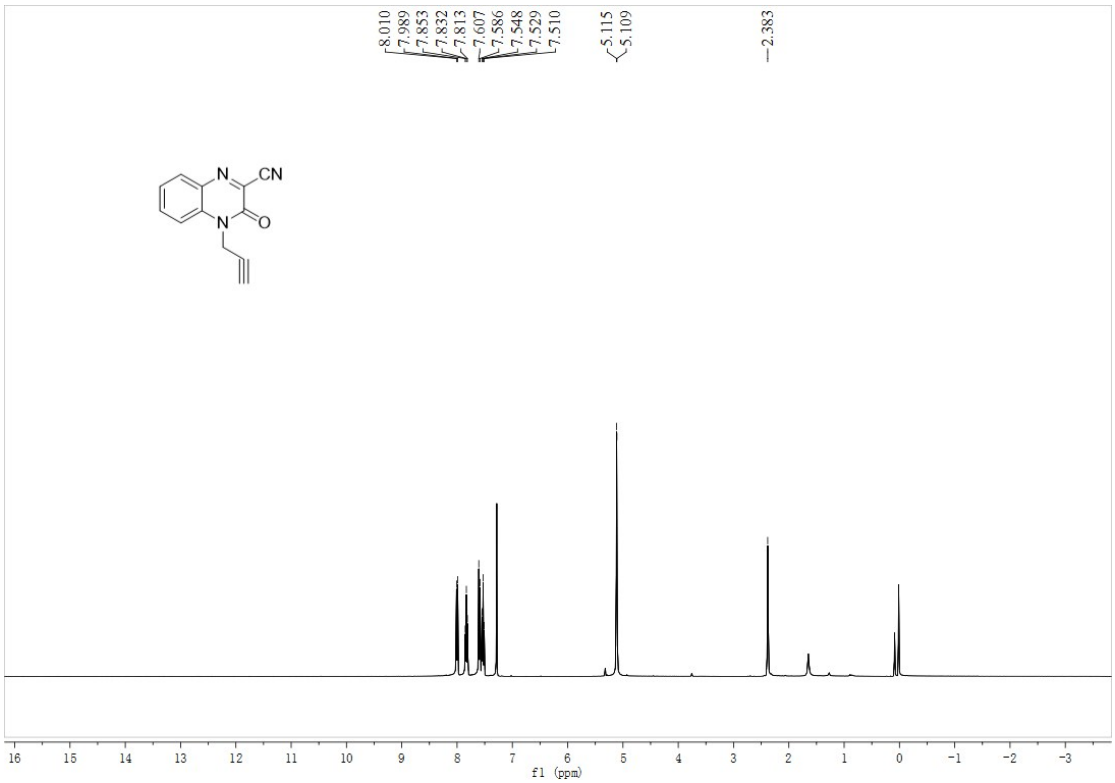


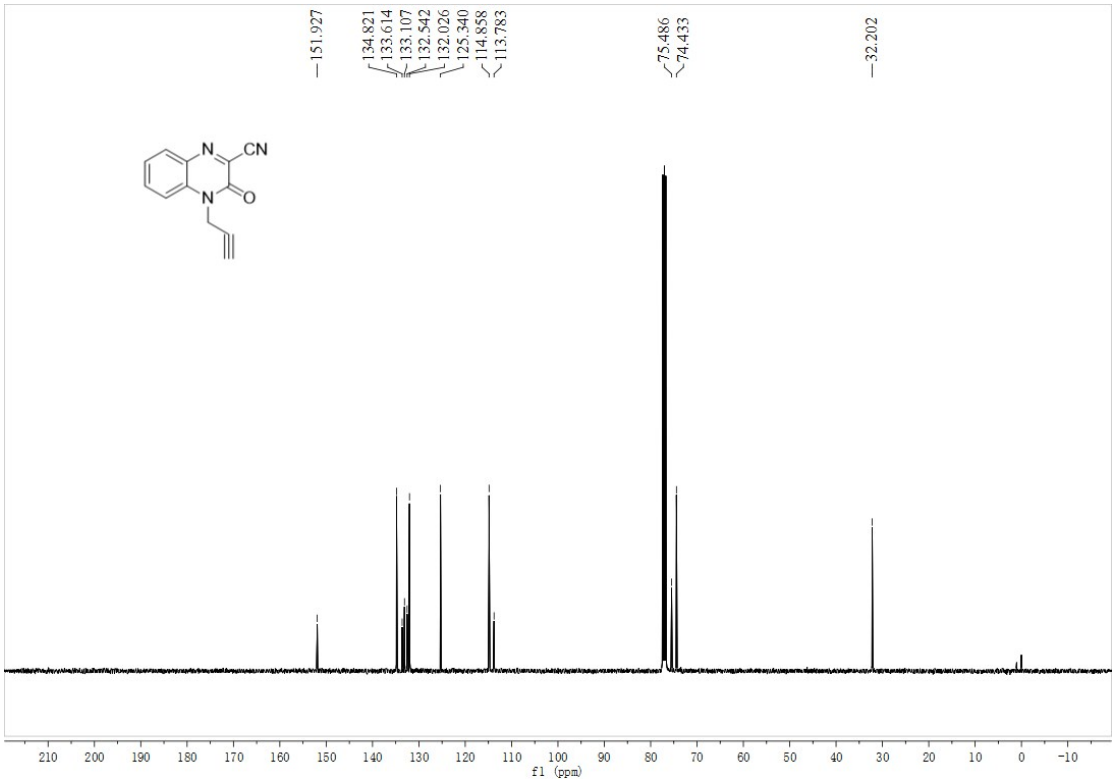
4-allyl-3-oxo-3,4-dihydroquinoxaline-2-carbonitrile (3am)



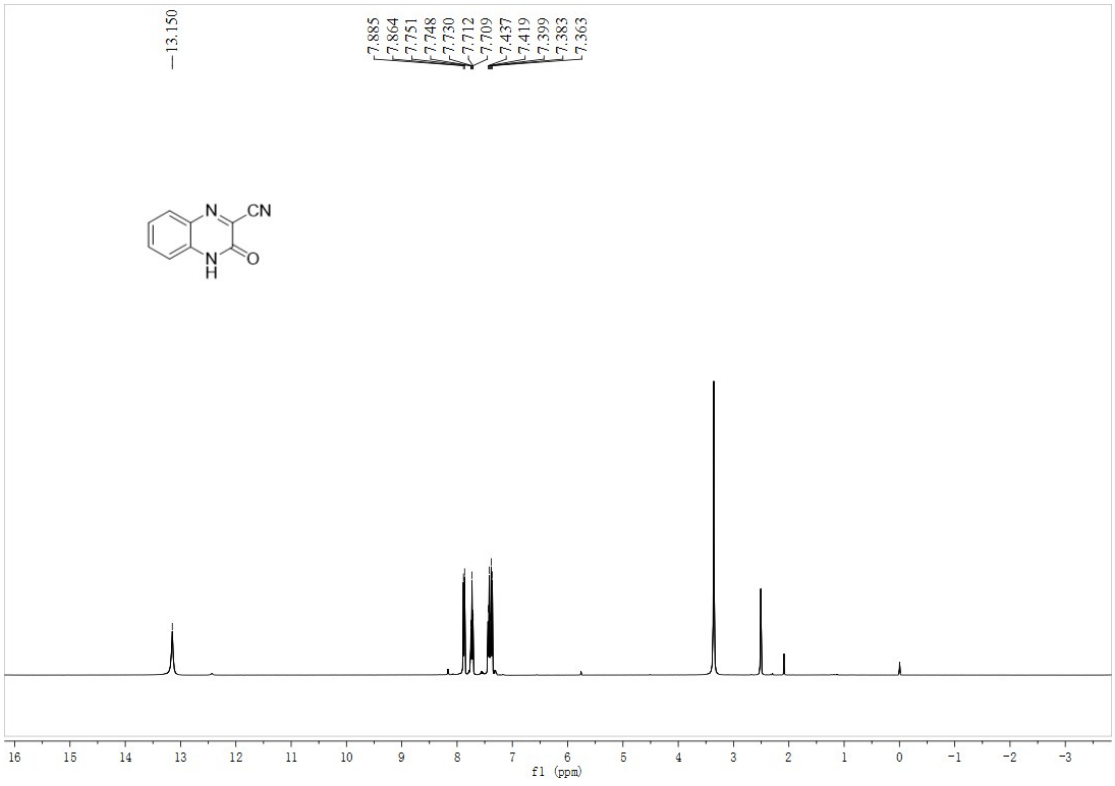


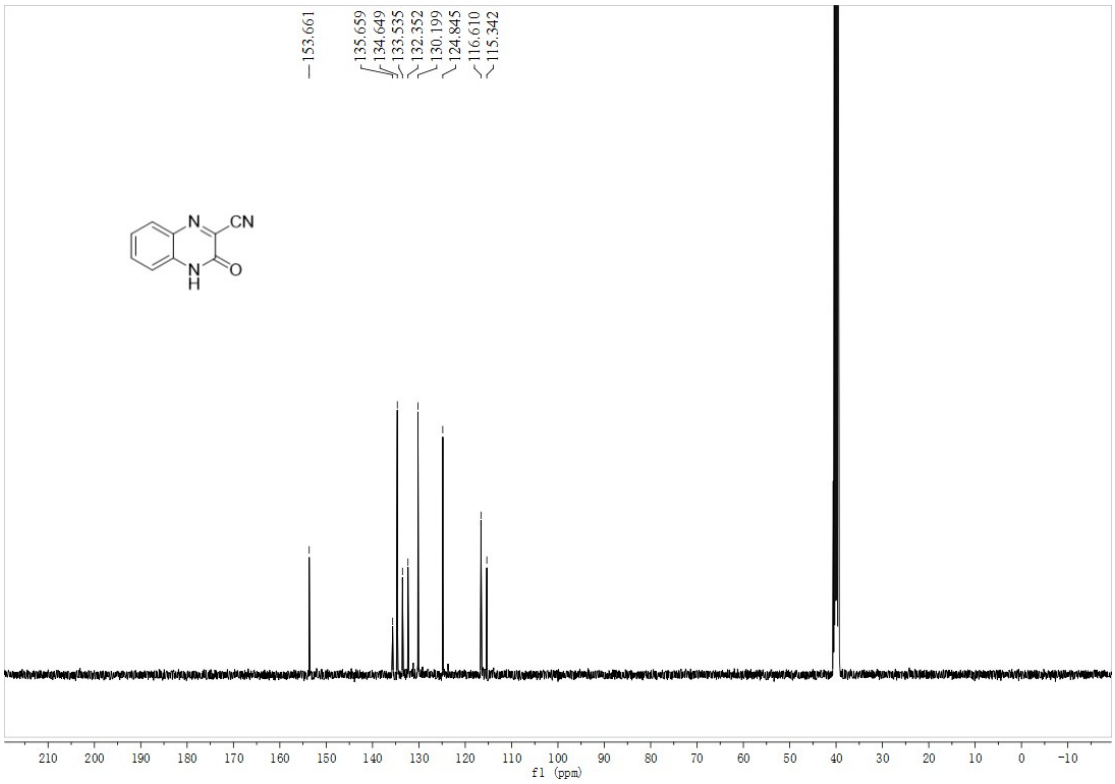
3-oxo-4-(*prop*-2-yn-1-yl)-3,4-dihydroquinoxaline-2-carbonitrile (3an)


8.010
7.989
7.853
7.832
7.813
7.607
7.586
7.548
7.529
7.510
5.115
5.109
2.383
N
CN
N
O
f1 (ppm)

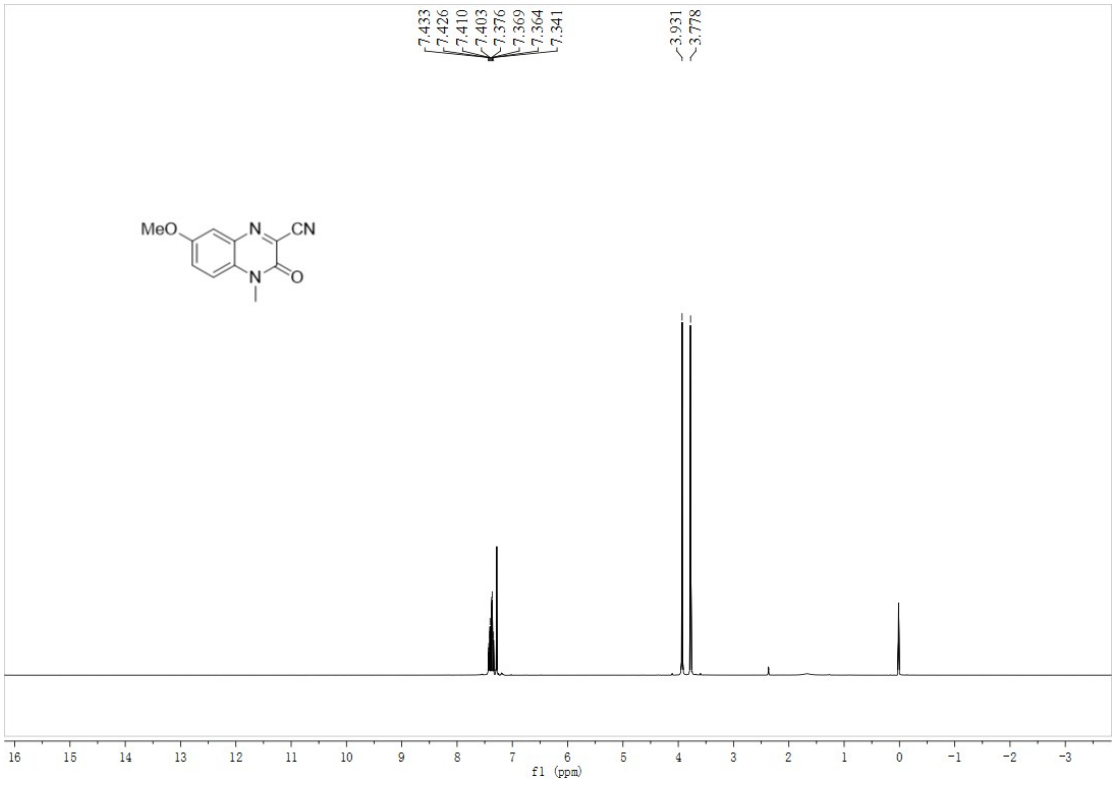

151.927
134.821
133.614
133.107
132.542
132.026
125.340
114.858
113.783
75.486
74.433
32.202
N
CN
N
O
f1 (ppm)

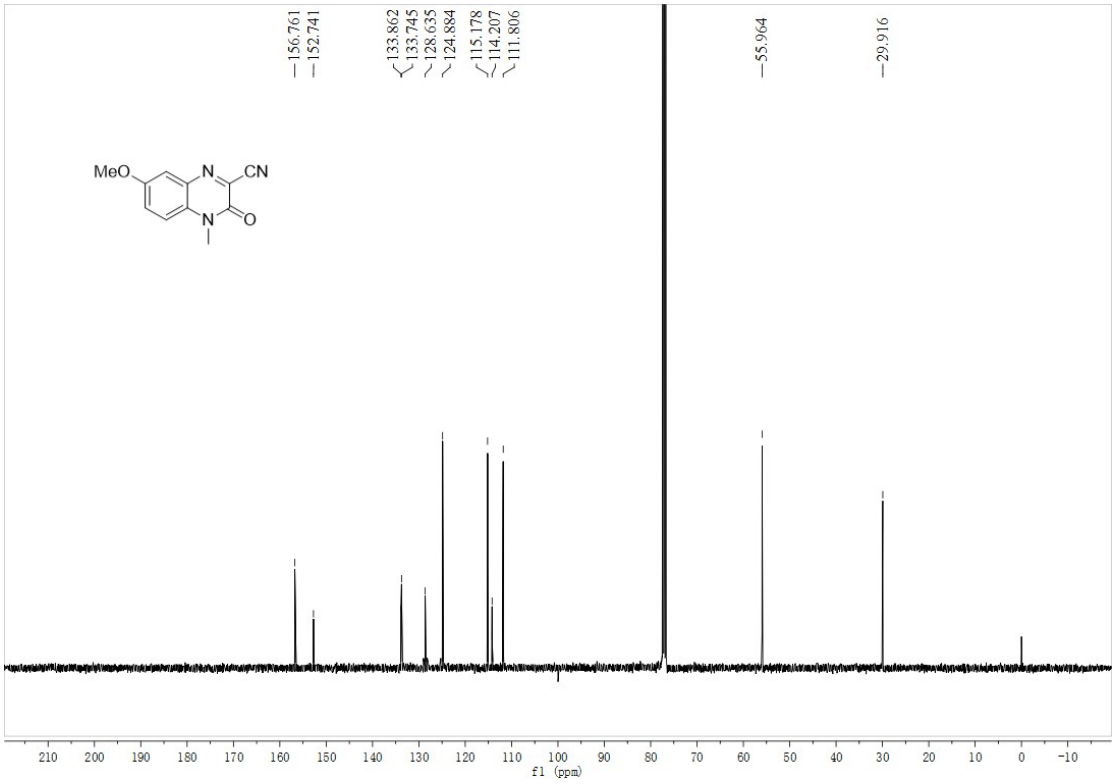
3-oxo-3,4-dihydroquinoxaline-2-carbonitrile (3ao)



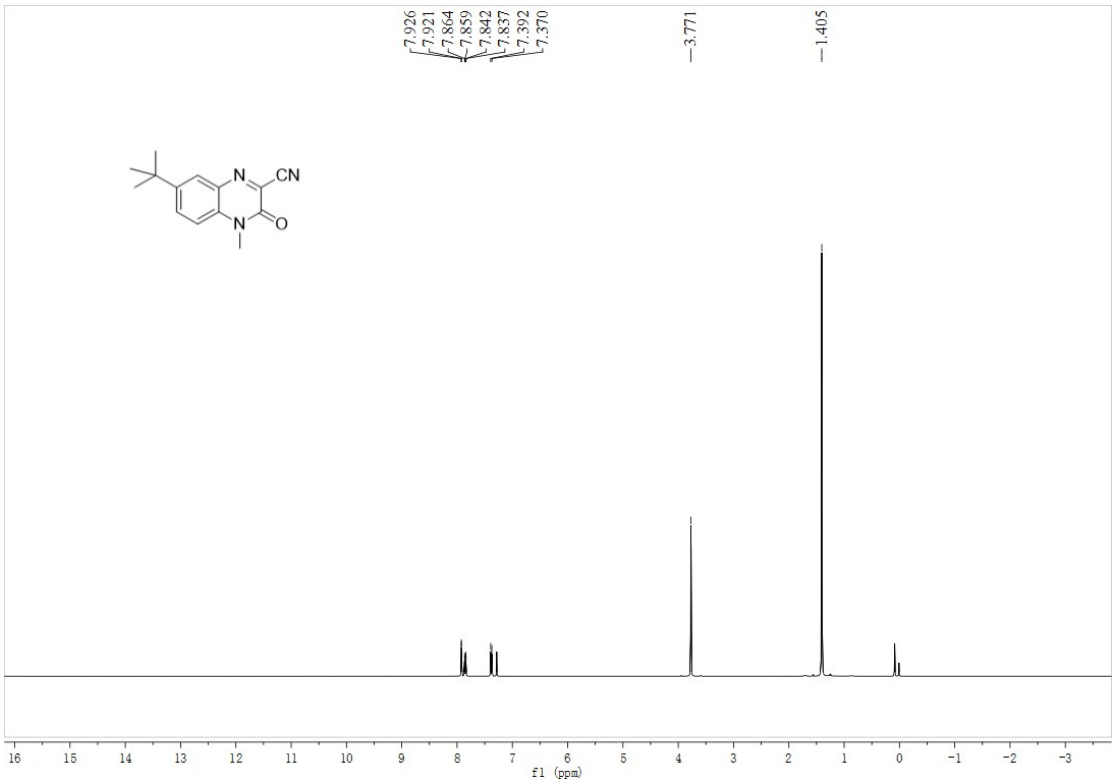


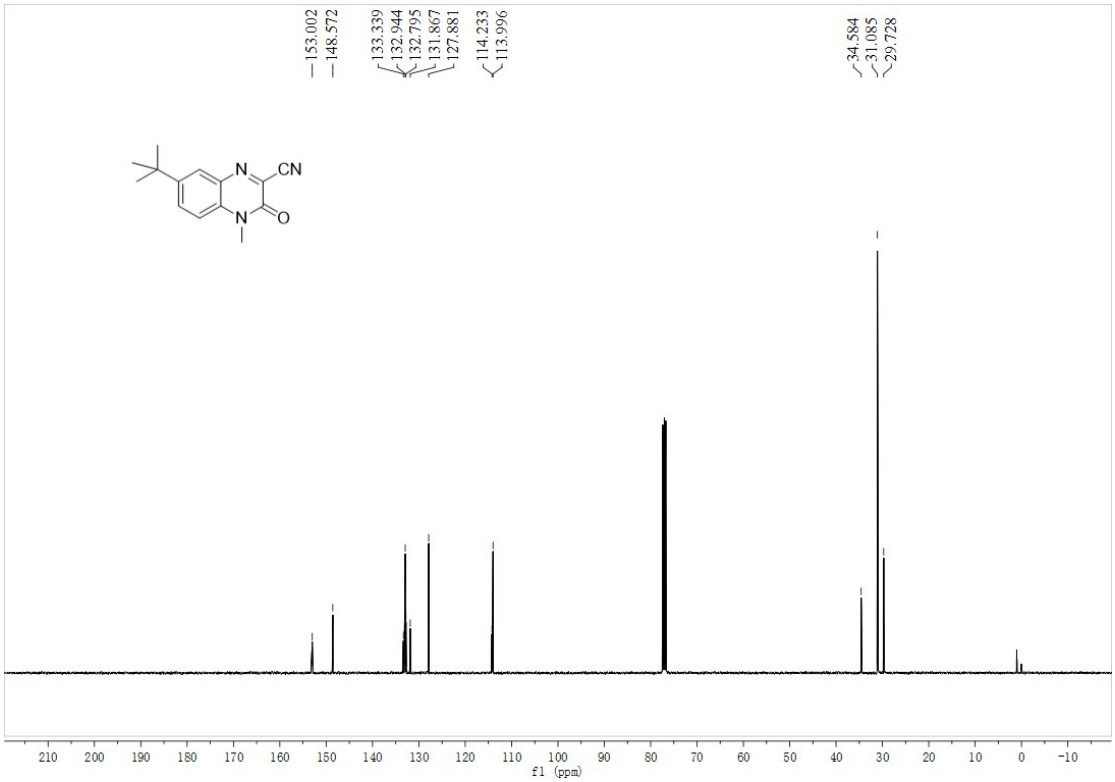
7-methoxy-4-methyl-3-oxo-3,4-dihydroquinoxaline-2-carbonitrile (3ba)



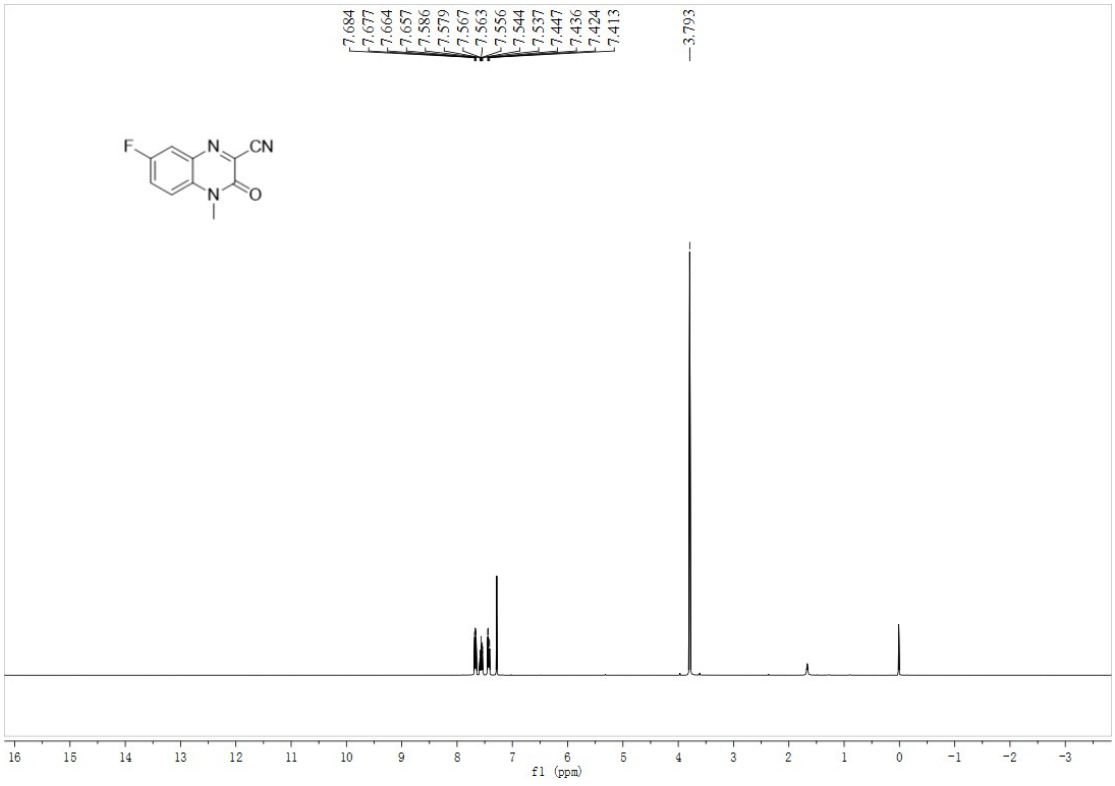


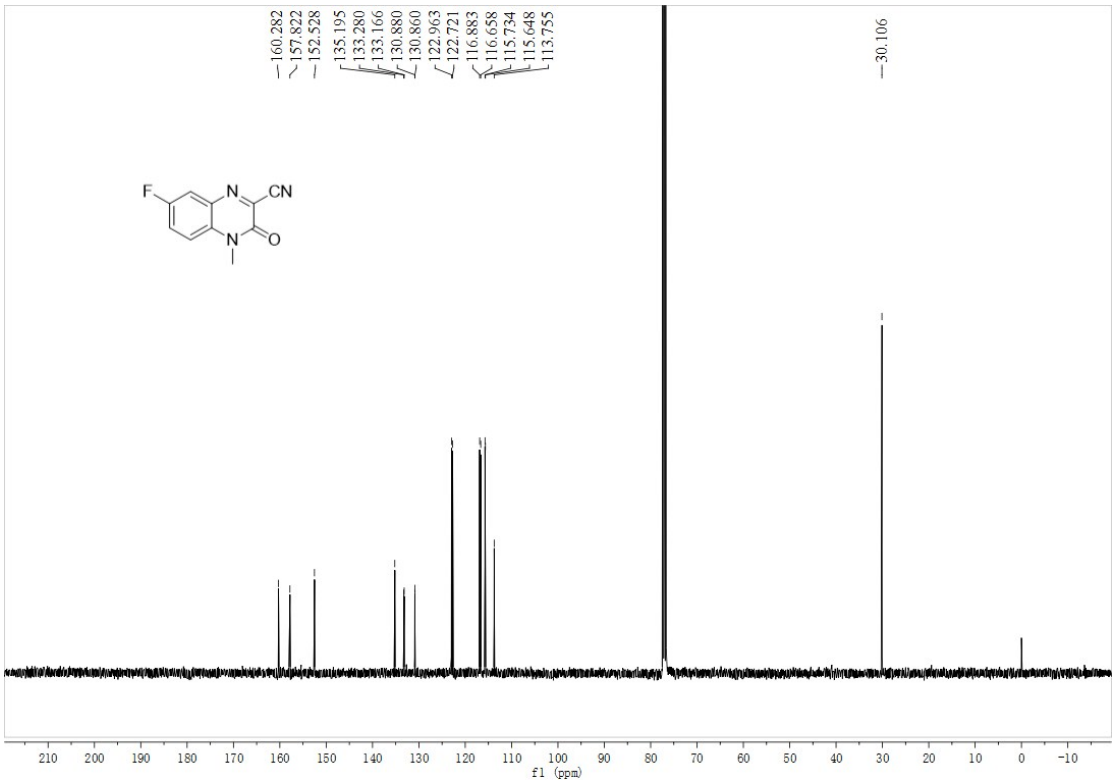
7-(*tert*-butyl)-4-methyl-3-oxo-3,4-dihydroquinoxaline-2-carbonitrile (3bb)

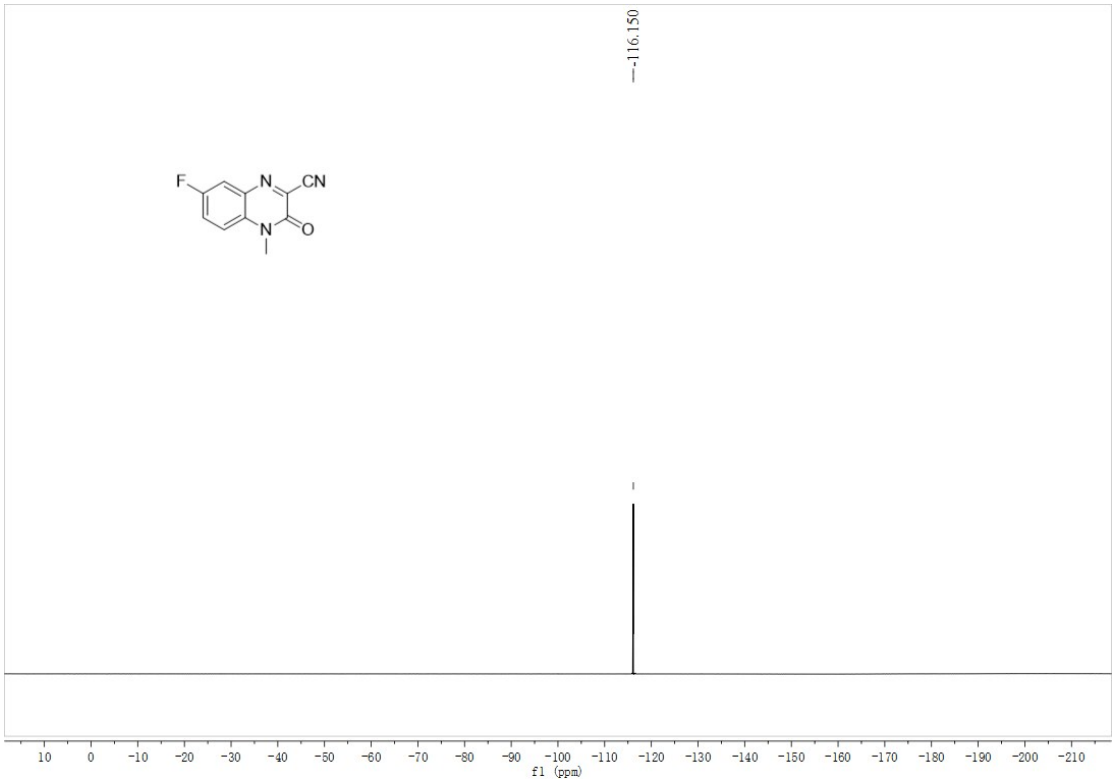

7.926
7.921
7.864
7.859
7.842
7.837
7.392
7.370
3.771
1.405
CN
N
O
f1 (ppm)


153.002
148.572
133.339
132.944
132.795
131.867
127.881
114.233
113.996
34.584
31.085
29.728
CN
N
O
f1 (ppm)

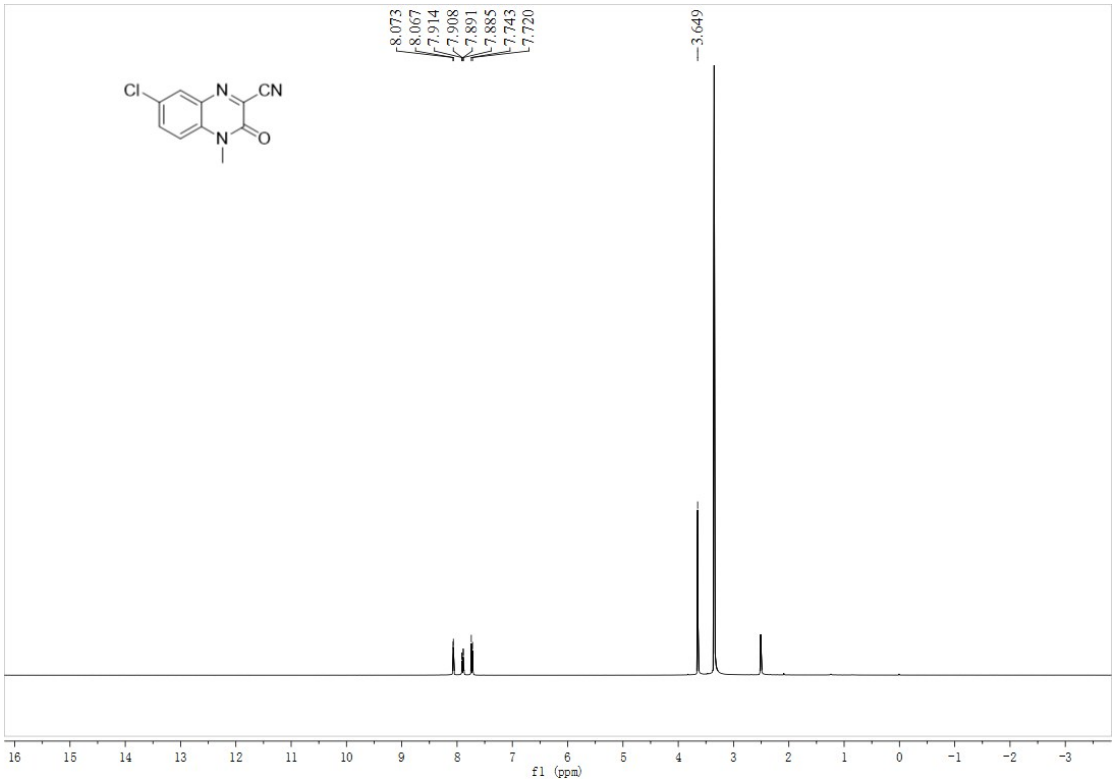
7-fluoro-4-methyl-3-oxo-3,4-dihydroquinoxaline-2-carbonitrile (3bc)

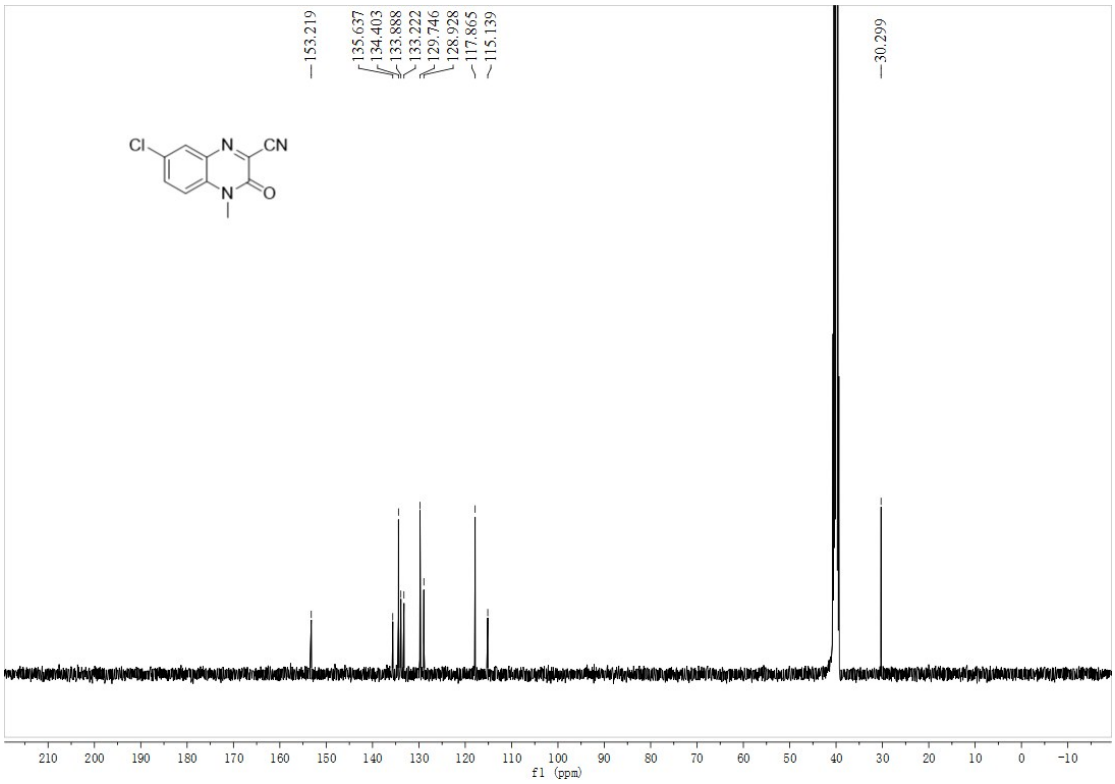



160.282
157.822
152.528
135.195
133.280
133.166
130.880
130.860
122.963
122.721
116.883
116.658
115.734
115.648
113.755
30.106
F
N
CN
N
O
f1 (ppm)

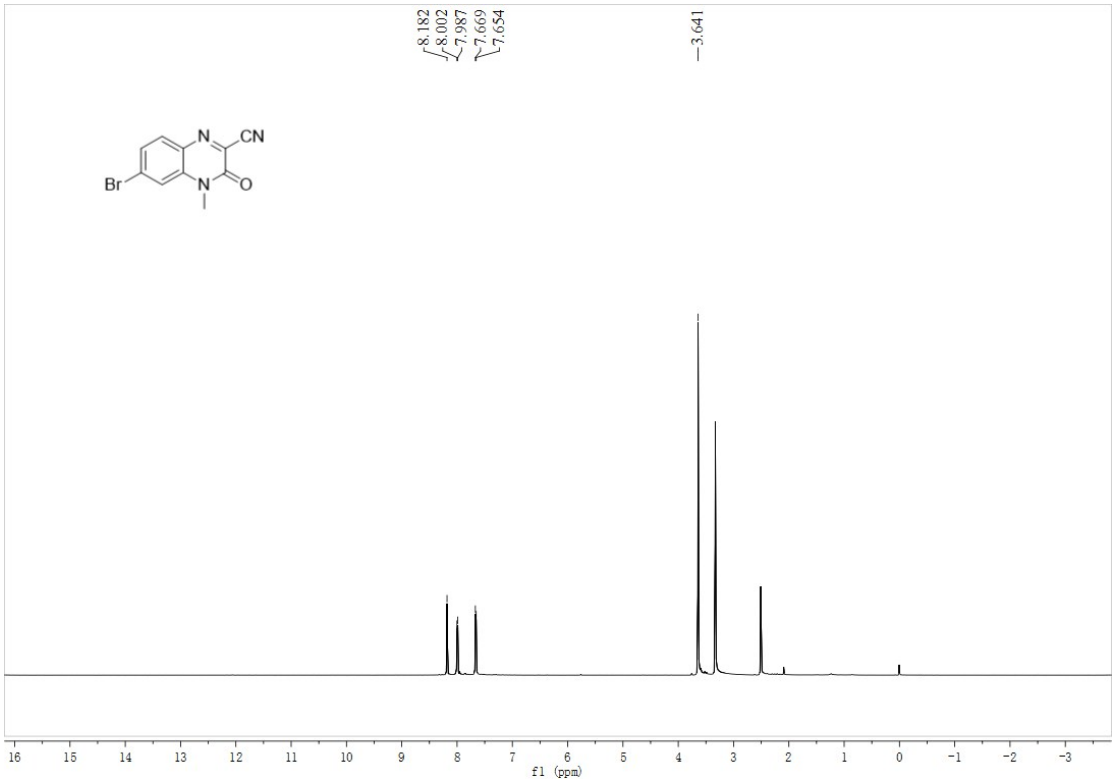

-116.150
F
N
CN
N
O
f1 (ppm)

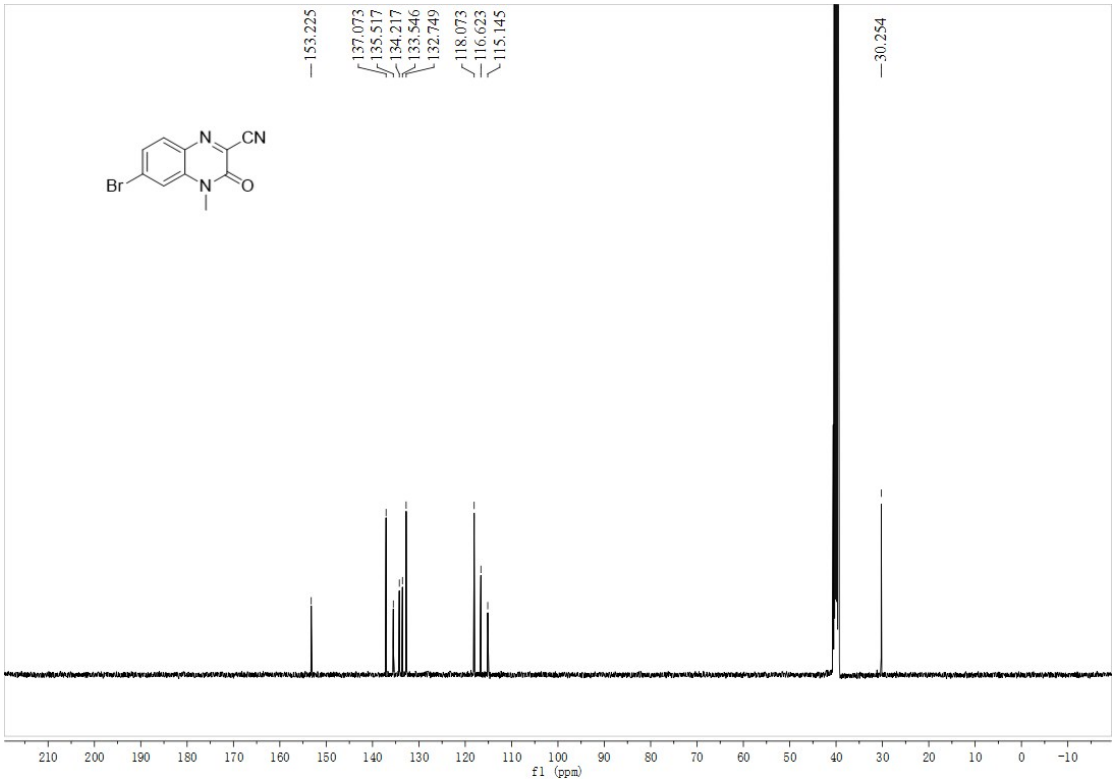
7-chloro-4-methyl-3-oxo-3,4-dihydroquinoxaline-2-carbonitrile (3bd)



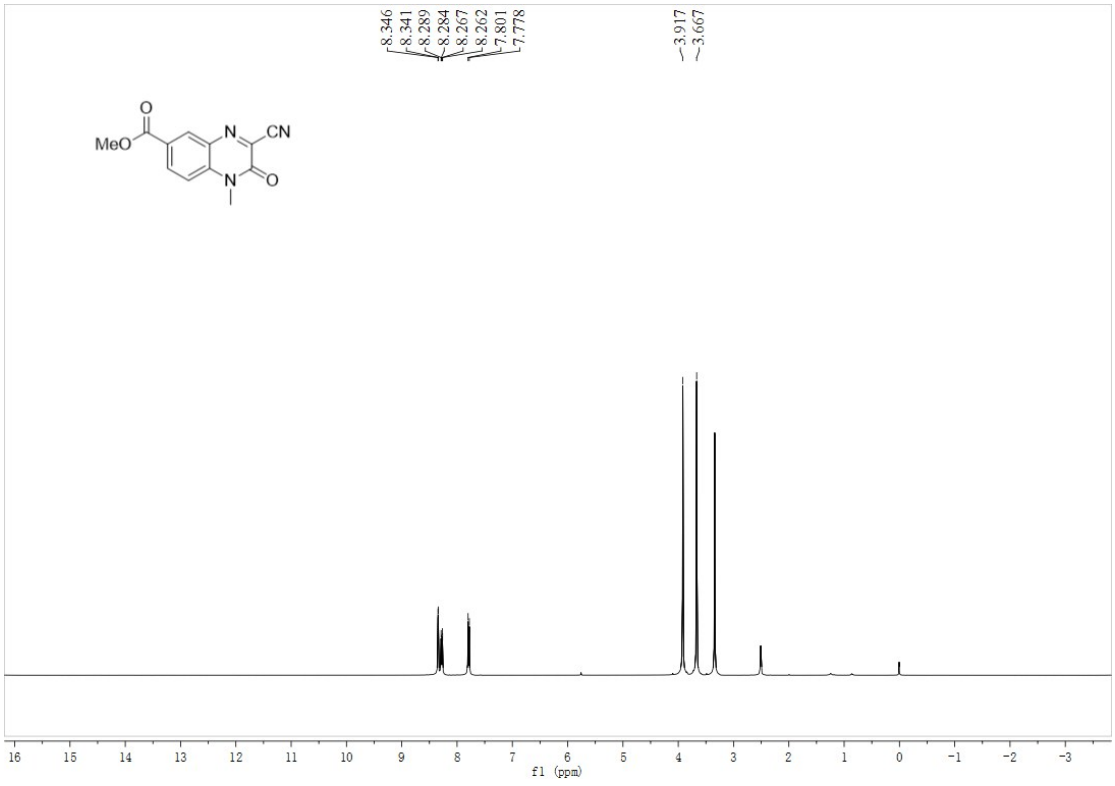


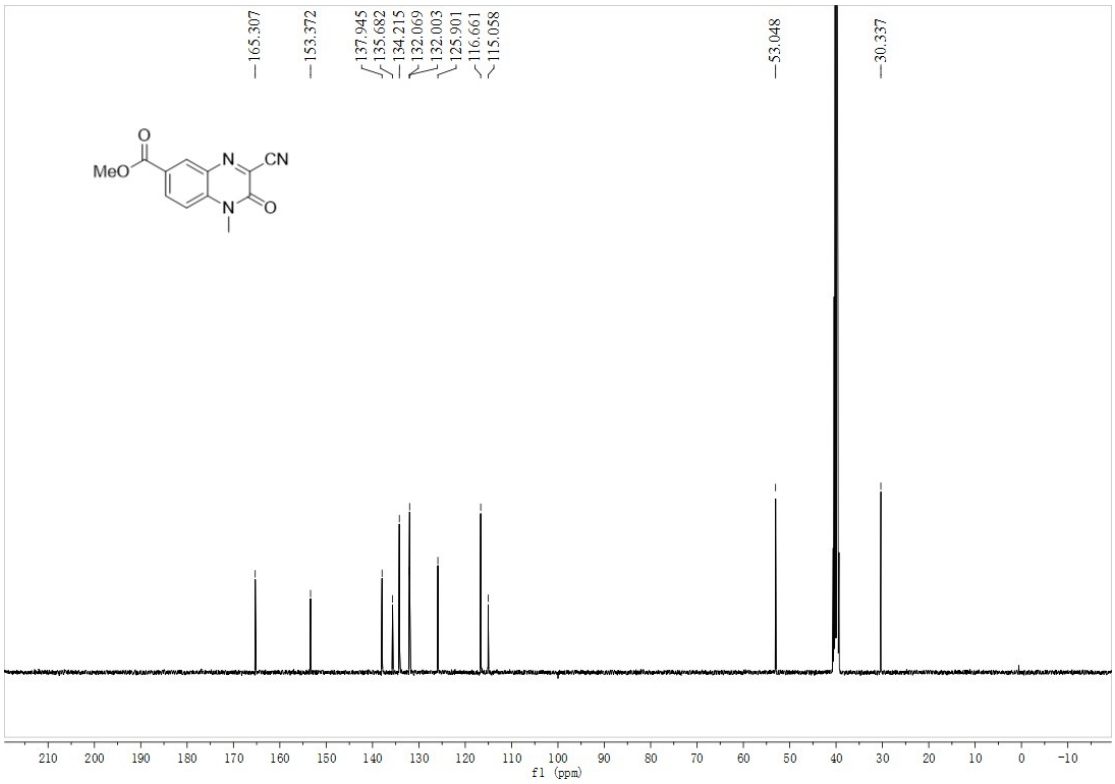
7-bromo-4-methyl-3-oxo-3,4-dihydroquinoxaline-2-carbonitrile (3be)


8.182
8.002
7.987
7.669
7.654
3.641
N
CN
Br
N
O
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

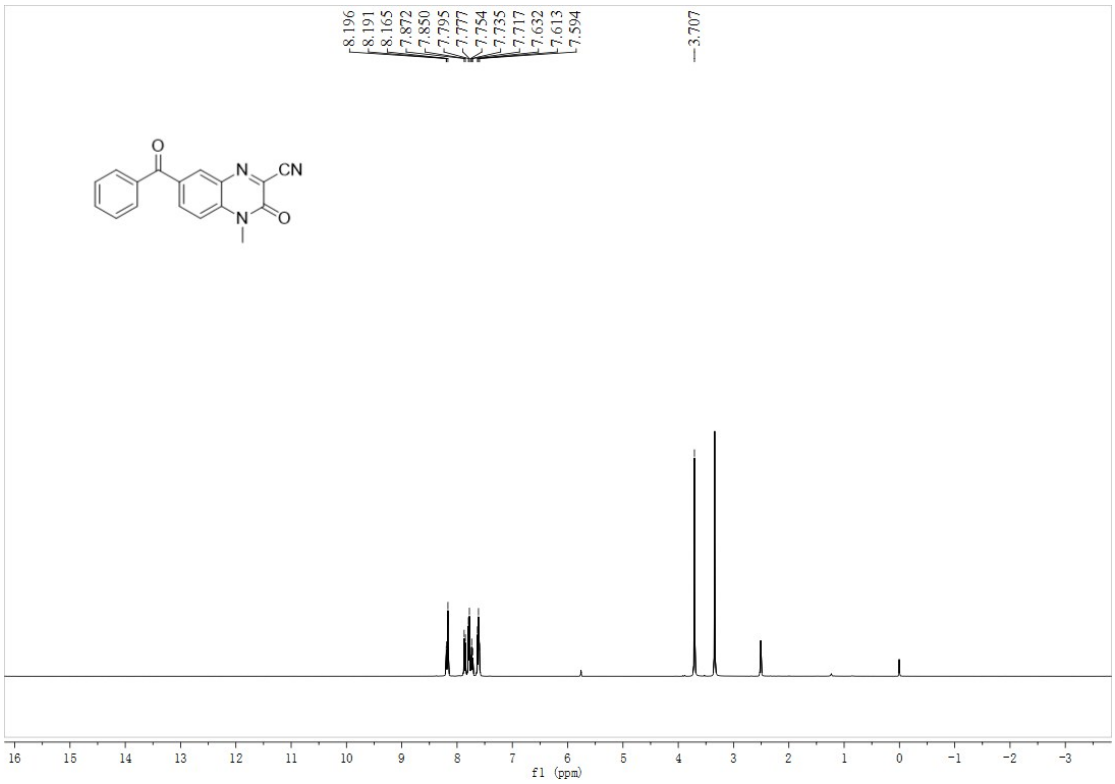

153.225
137.073
135.517
134.217
133.546
132.749
118.073
116.623
115.145
30.254
N
CN
Br
N
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

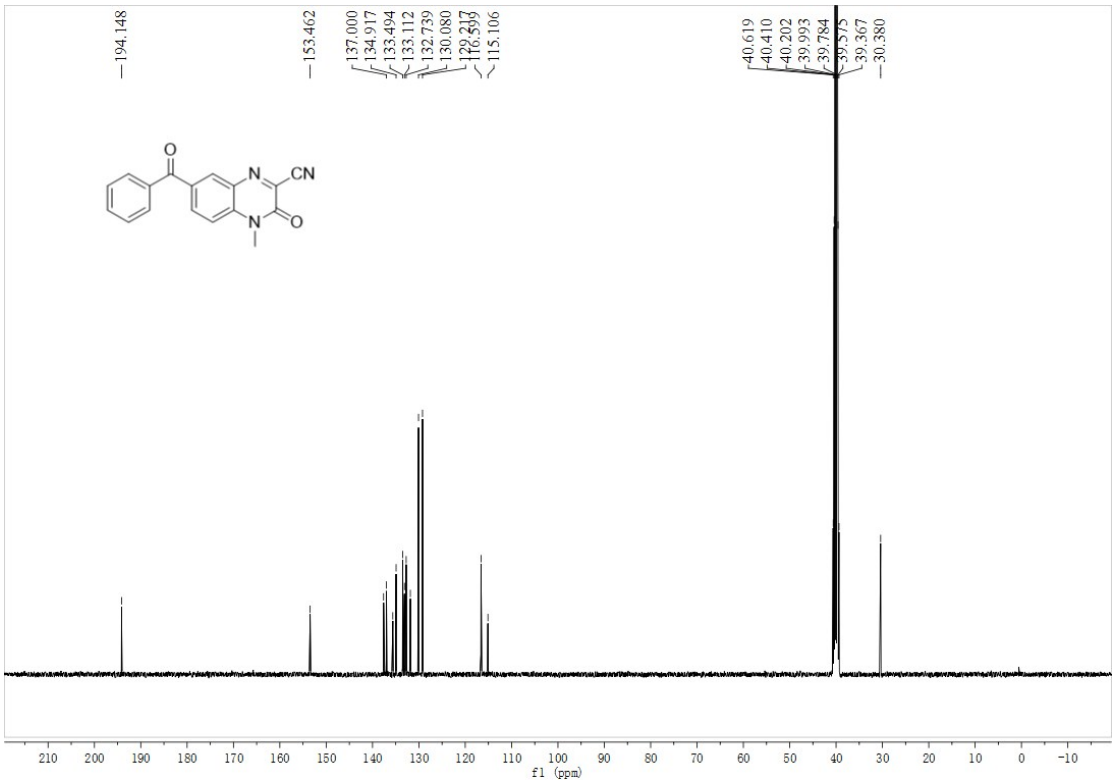
methyl 3-cyano-1-methyl-2-oxo-1,2-dihydroquinoxaline-6-carboxylate (3bf)



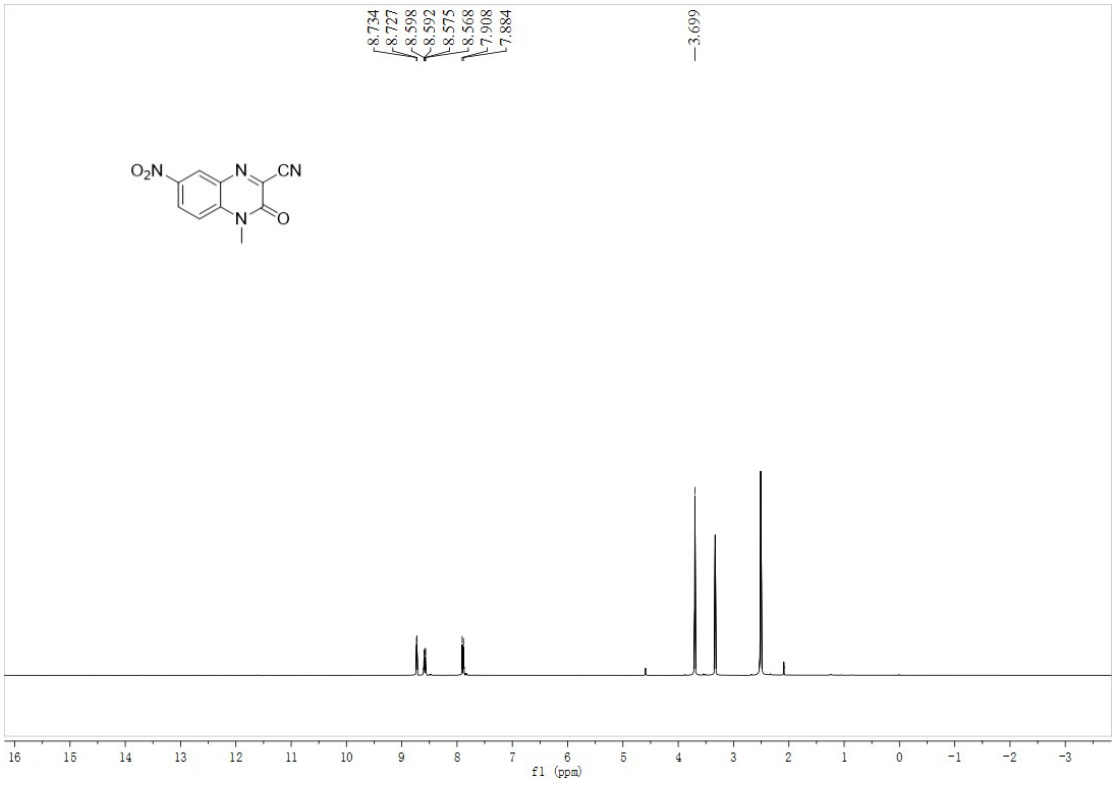


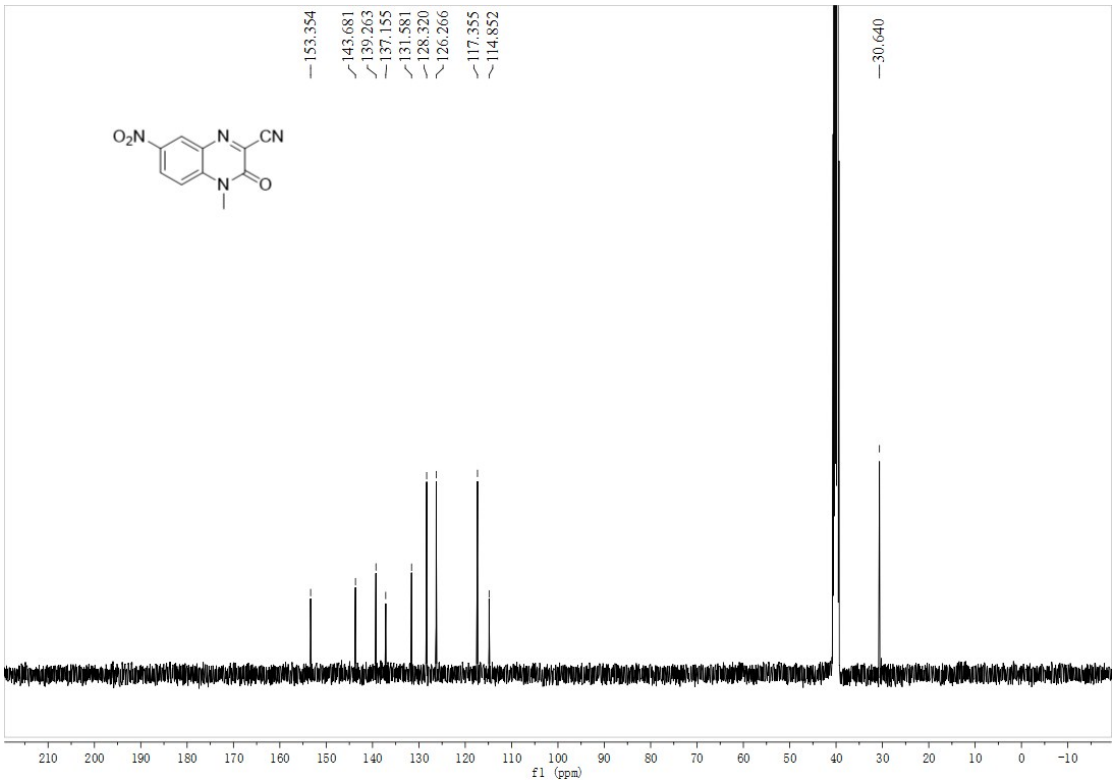
7-benzoyl-4-methyl-3-oxo-3,4-dihydroquinoxaline-2-carbonitrile (3bg)


8.196
8.191
8.165
7.872
7.850
7.795
7.777
7.754
7.735
7.717
7.632
7.613
7.594
3.707
O
N
CN
N
O
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

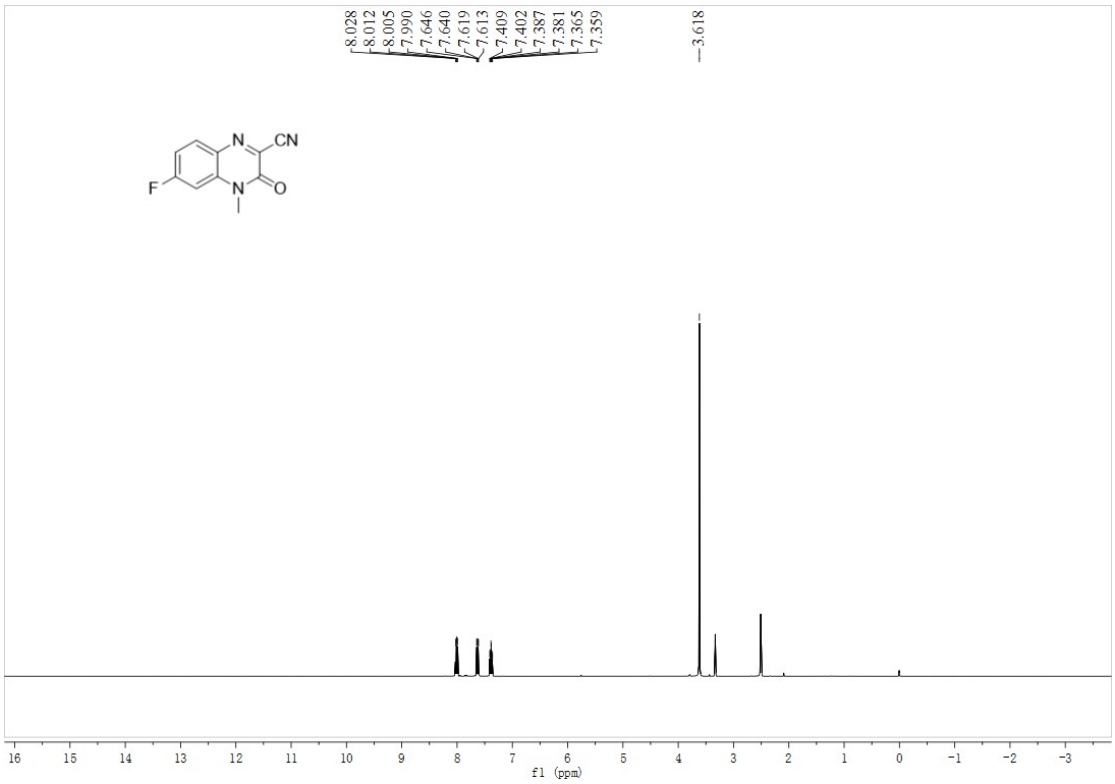

194.148
153.462
137.000
134.917
133.494
133.112
132.739
130.080
129.217
115.106
40.619
40.410
40.202
39.993
39.784
39.575
39.367
30.380
O
N
CN
N
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

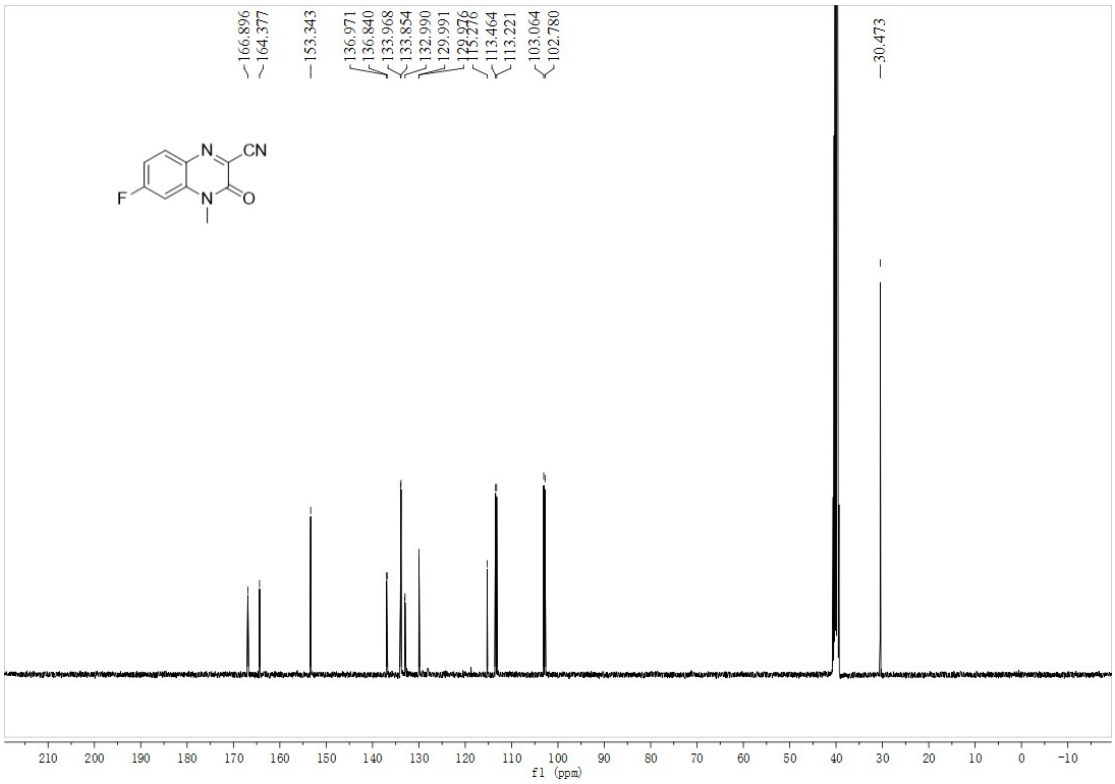
4-methyl-7-nitro-3-oxo-3,4-dihydroquinoxaline-2-carbonitrile (3bh)

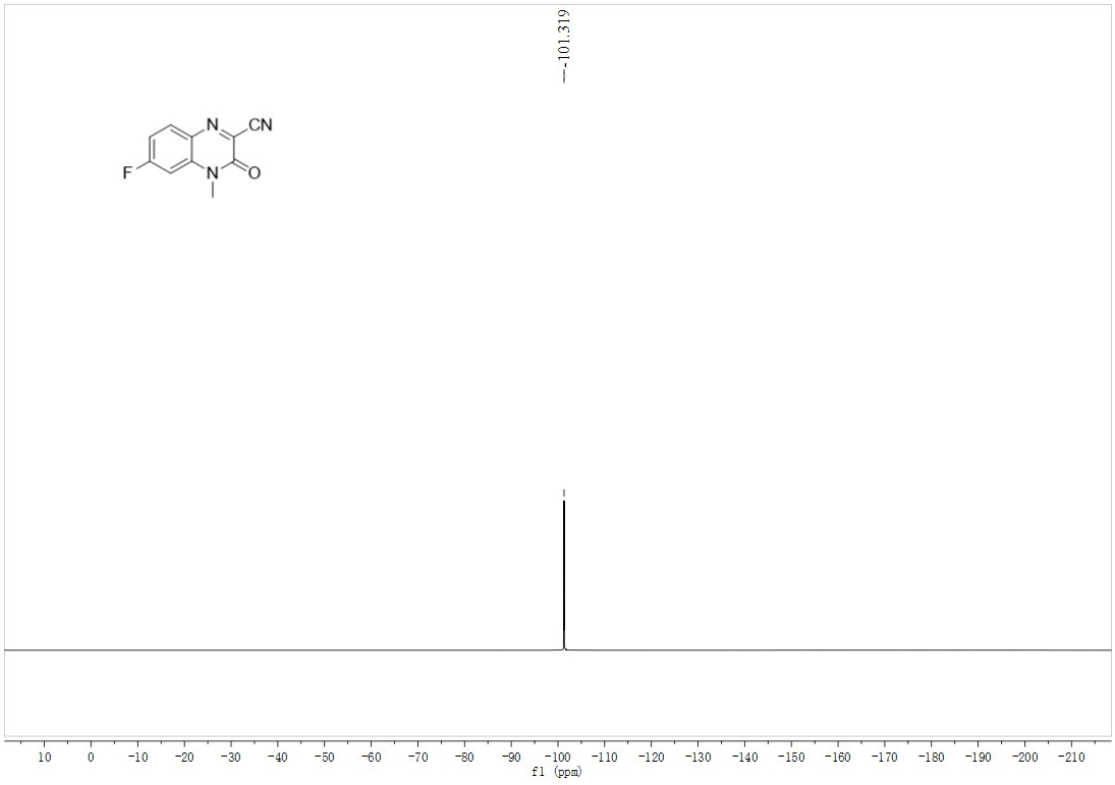




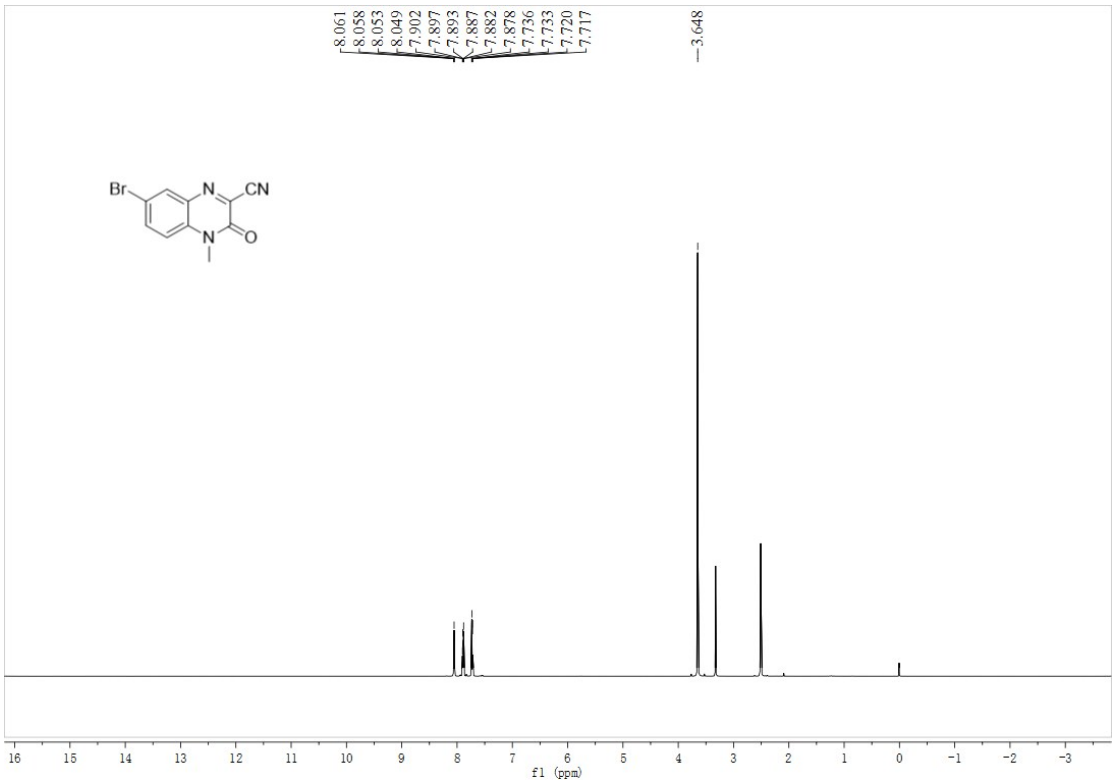
6-fluoro-4-methyl-3-oxo-3,4-dihydroquinoxaline-2-carbonitrile (3bi)

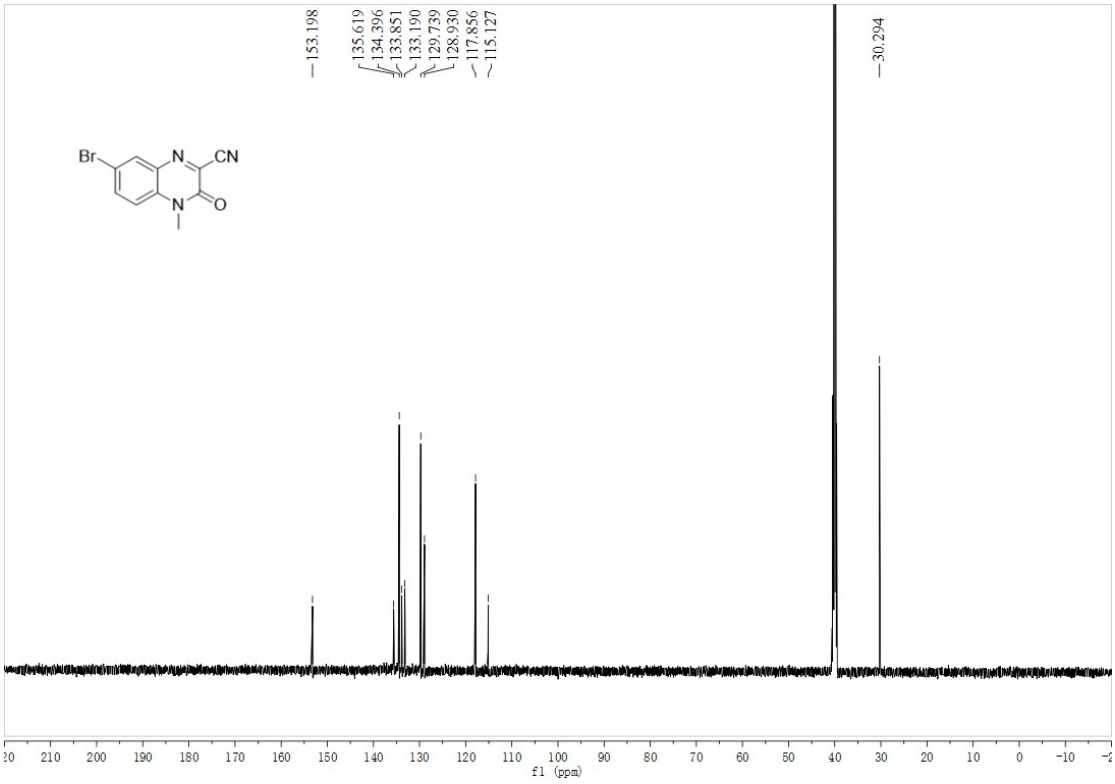

8.028
8.012
8.005
7.990
7.646
7.640
7.619
7.613
7.409
7.402
7.387
7.381
7.365
7.359
3.618
N
CN
F
N
O
f1 (ppm)


166.896
164.377
153.343
136.971
136.840
133.968
133.854
132.990
129.991
129.976
115.276
113.464
113.221
103.064
102.780
30.473
N
CN
F
N
O
f1 (ppm)

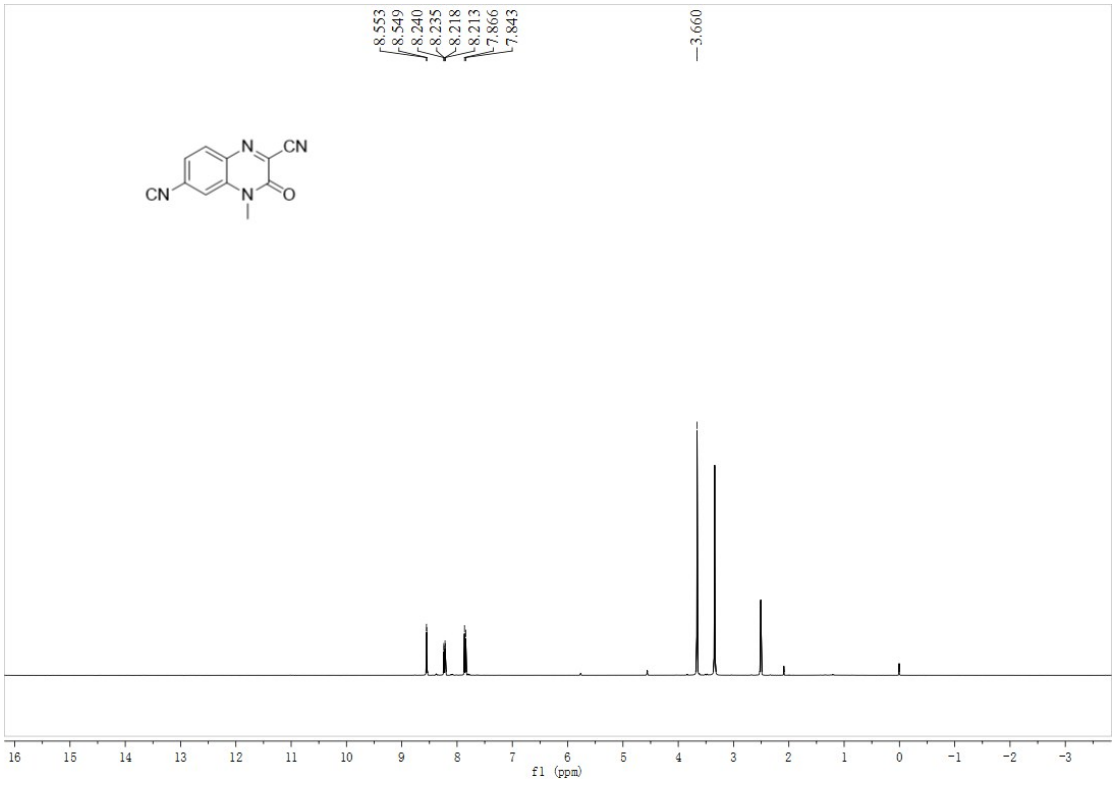


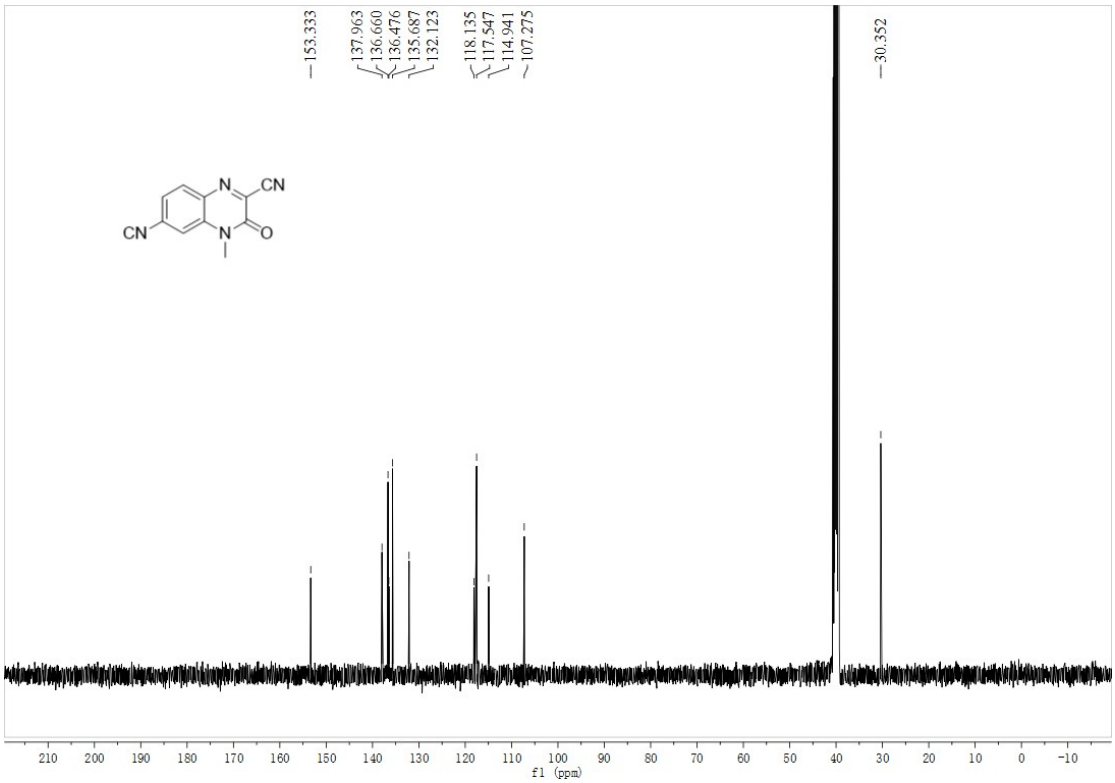
6-bromo-4-methyl-3-oxo-3,4-dihydroquinoxaline-2-carbonitrile (3bj)


8.061
8.058
8.053
8.049
7.902
7.897
7.893
7.887
7.882
7.878
7.736
7.733
7.720
7.717
3.648
Br
N
CN
N
O
f1 (ppm)

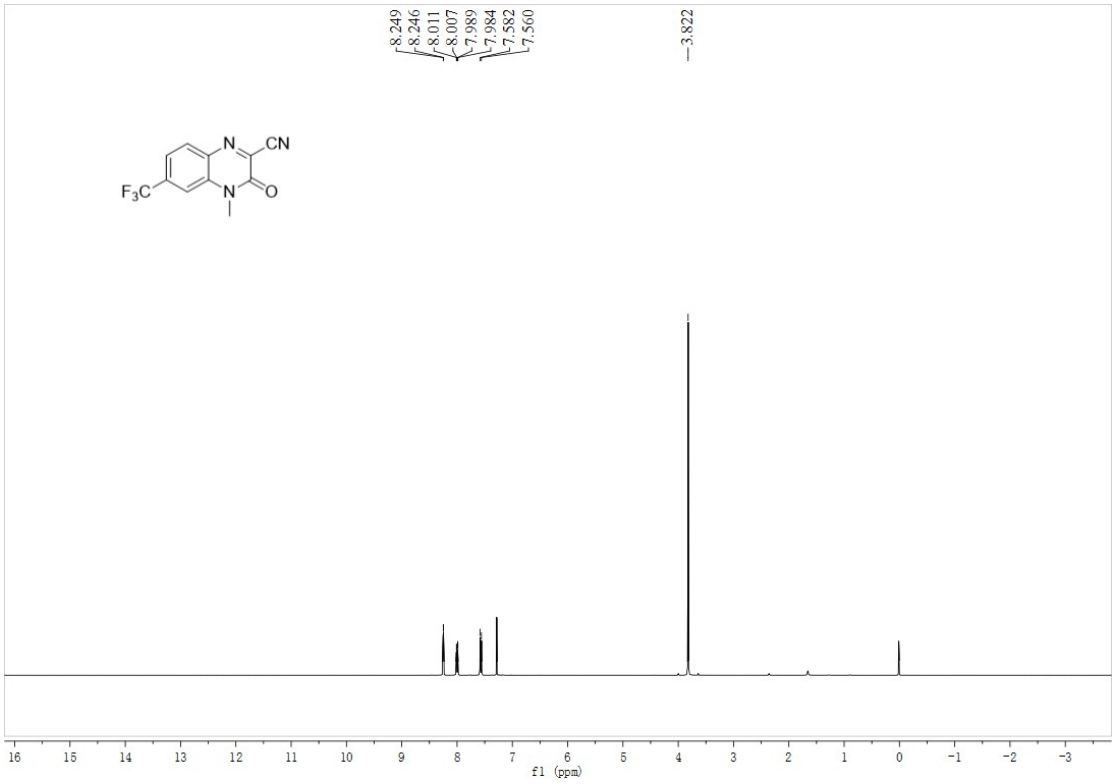

153.198
135.619
134.396
133.851
133.190
129.739
128.930
117.856
115.127
30.294
Br
N
CN
N
O
f1 (ppm)

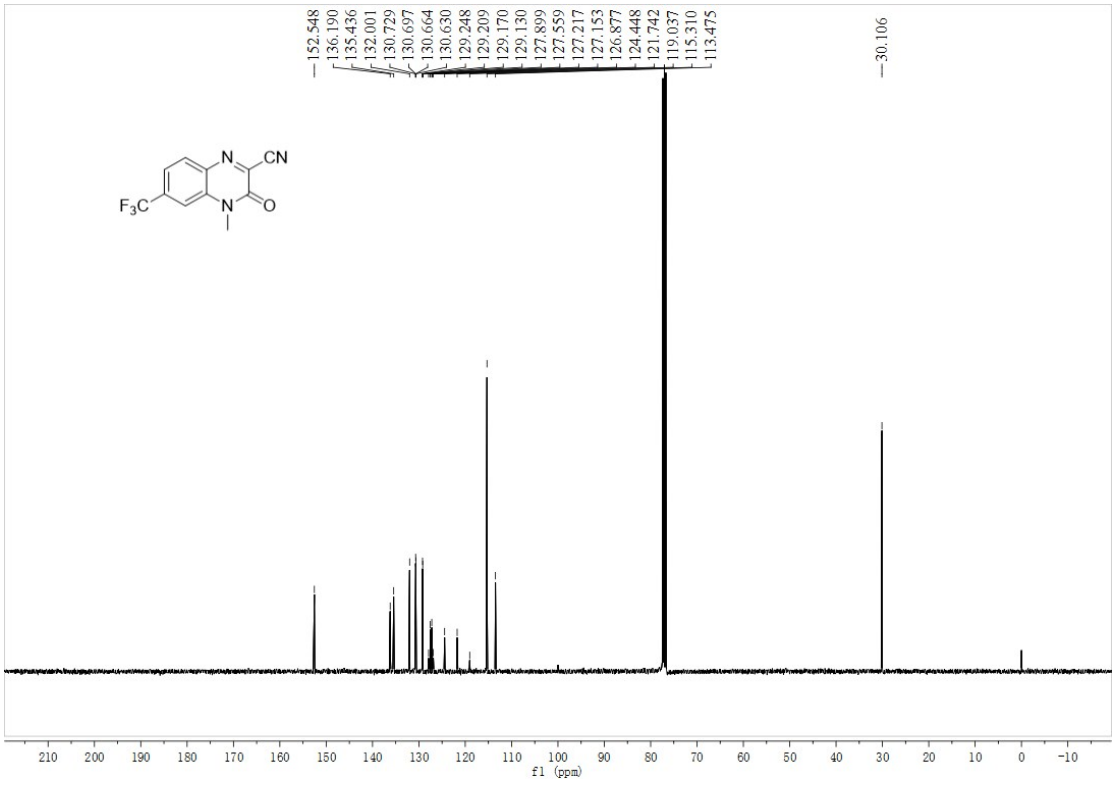
6-isocyano-4-methyl-3-oxo-3,4-dihydroquinoxaline-2-carbonitrile (3bk)

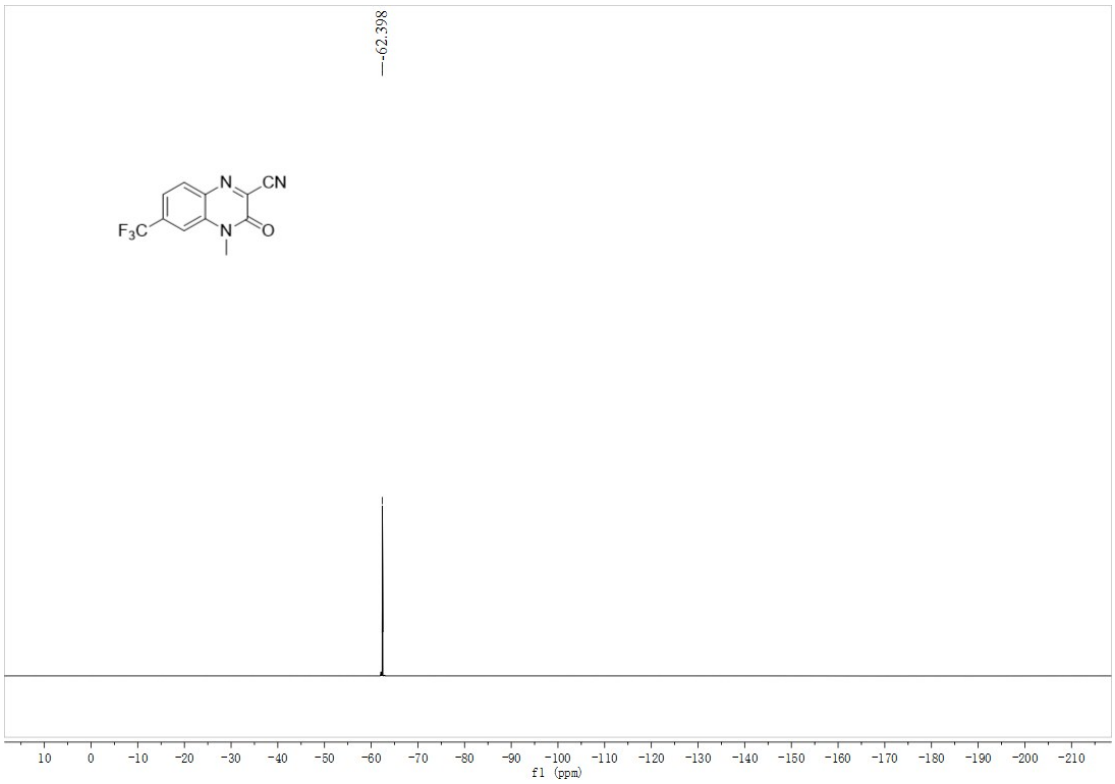




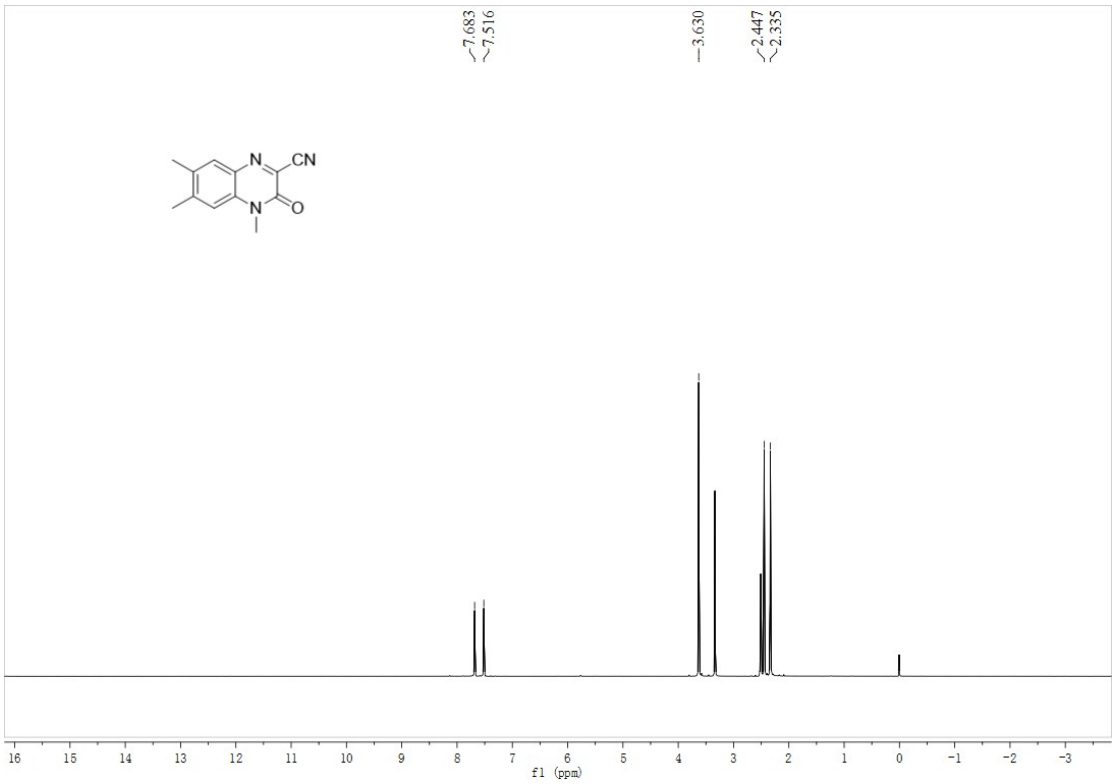
4-methyl-3-oxo-6-(trifluoromethyl)-3,4-dihydroquinoxaline-2-carbonitrile (3bl)

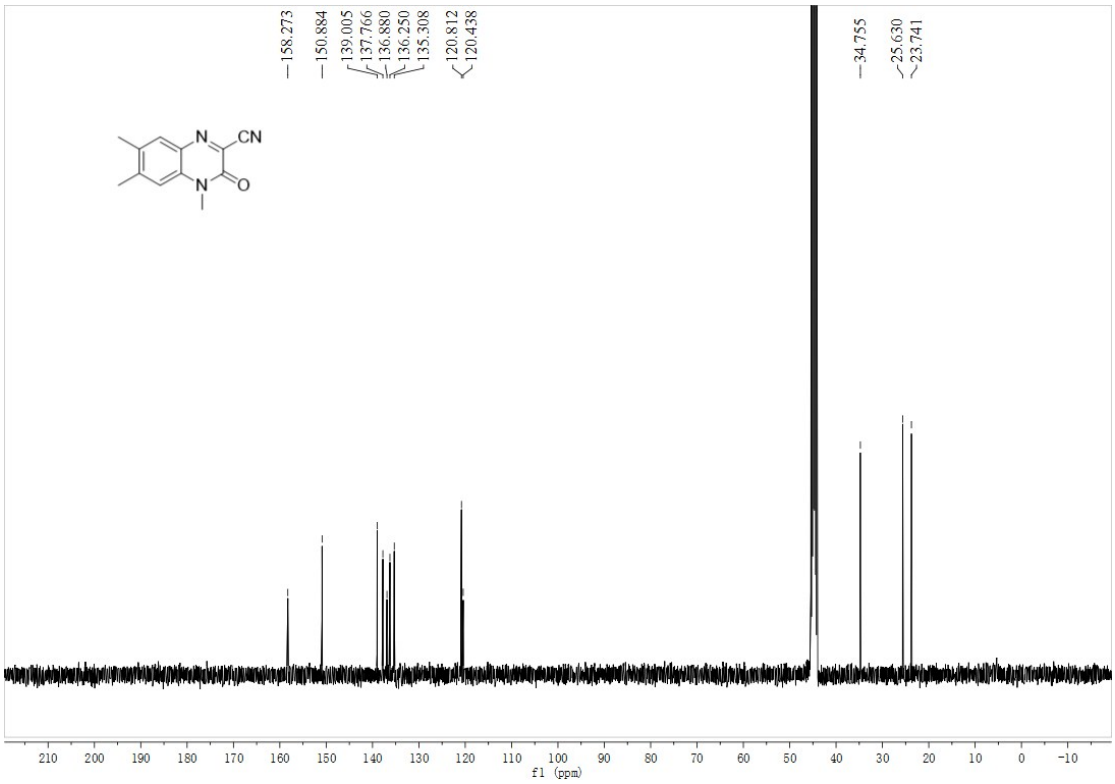



152.548
136.190
135.436
132.001
130.729
130.697
130.664
130.630
129.248
129.209
129.170
129.130
127.899
127.559
127.217
127.153
126.877
124.448
121.742
119.037
115.310
113.475
30.106
CN
F3C
N
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

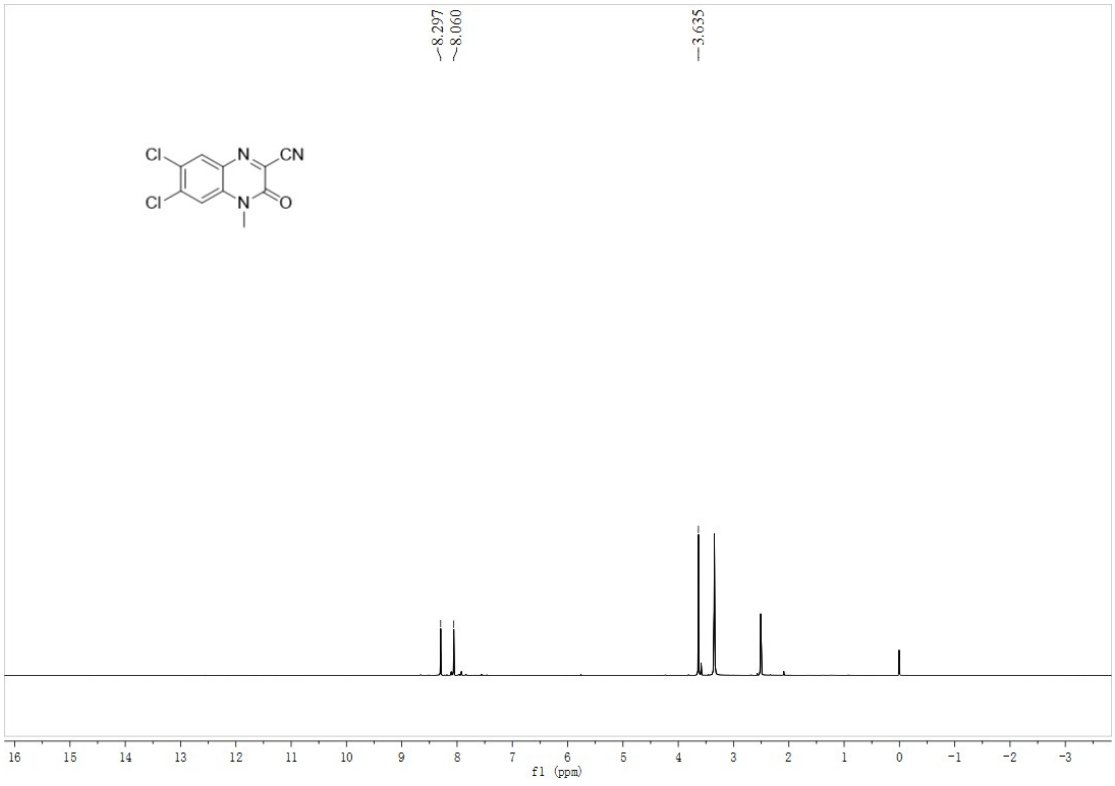


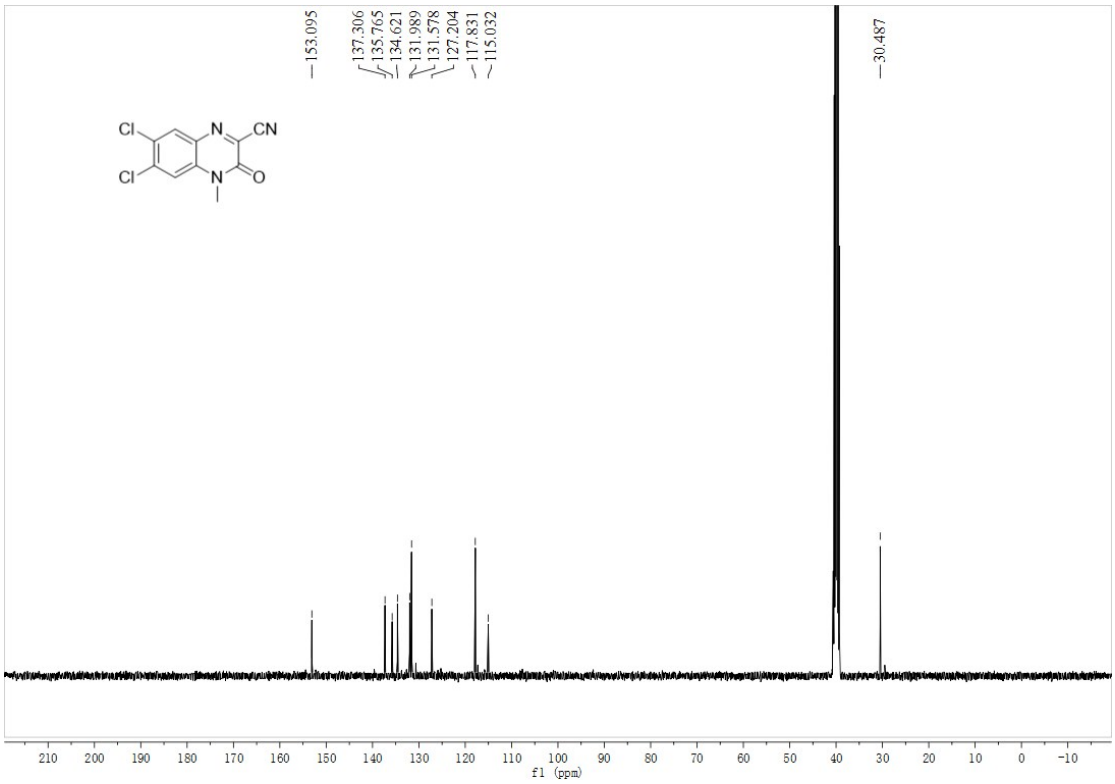
4,6,7-trimethyl-3-oxo-3,4-dihydroquinoxaline-2-carbonitrile (3bm)


7.683
7.516
3.630
2.447
2.335
CN
O
f1 (ppm)

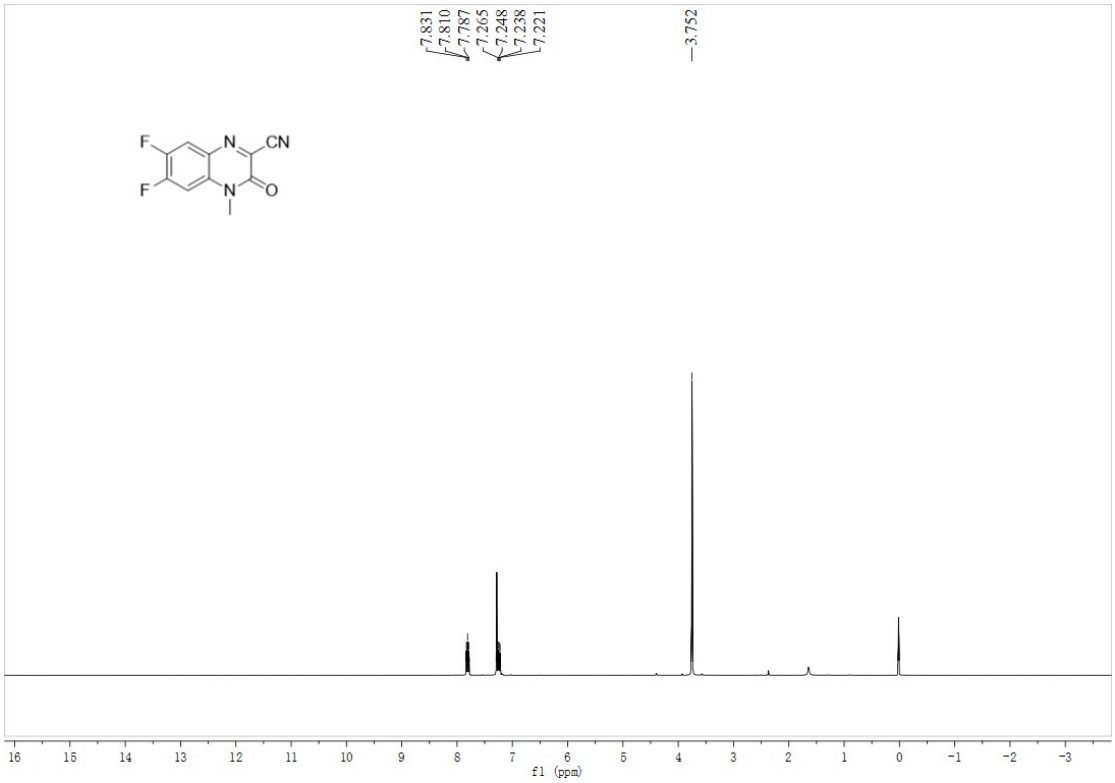

158.273
150.884
139.005
137.766
136.880
136.250
135.308
120.812
120.438
34.755
25.630
23.741
CN
O
f1 (ppm)

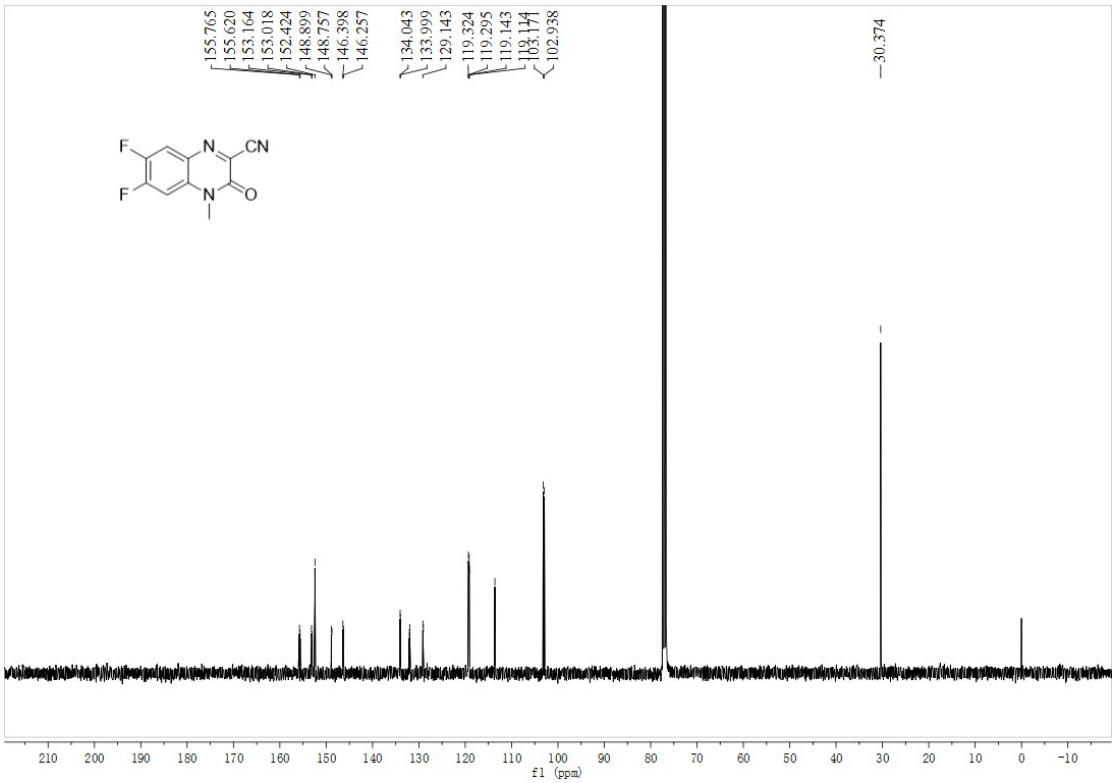
6,7-dichloro-4-methyl-3-oxo-3,4-dihydroquinoxaline-2-carbonitrile (3bn)

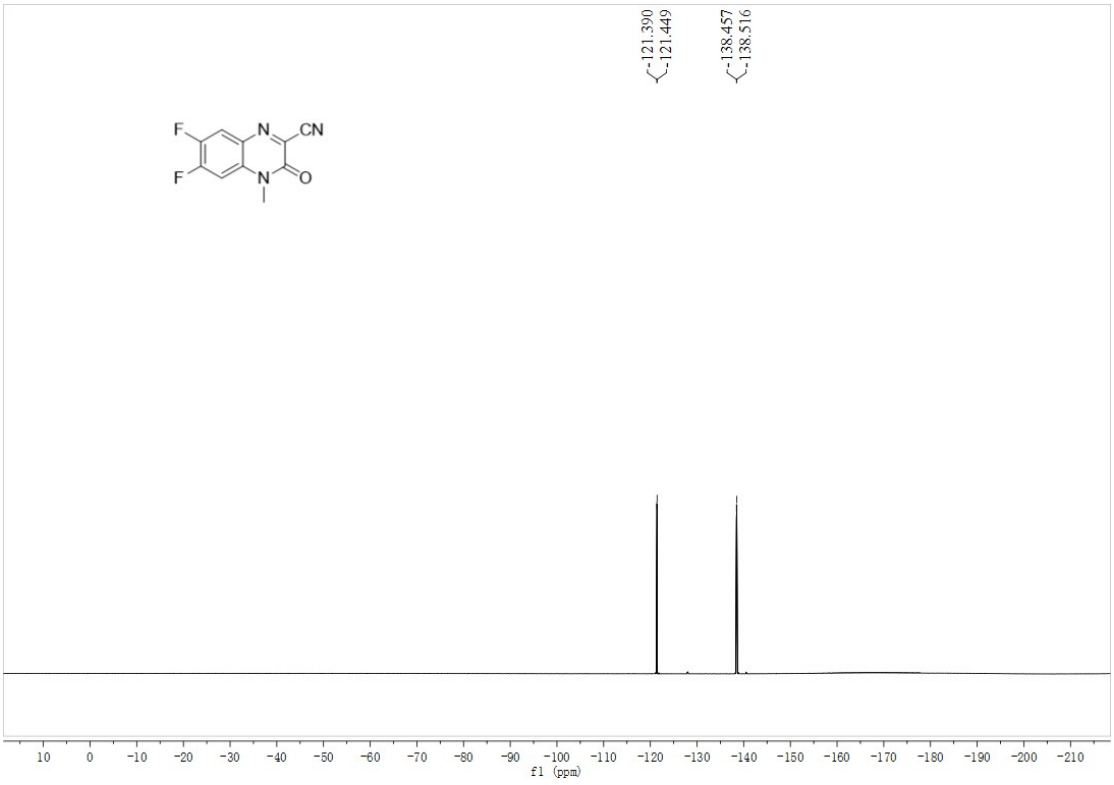




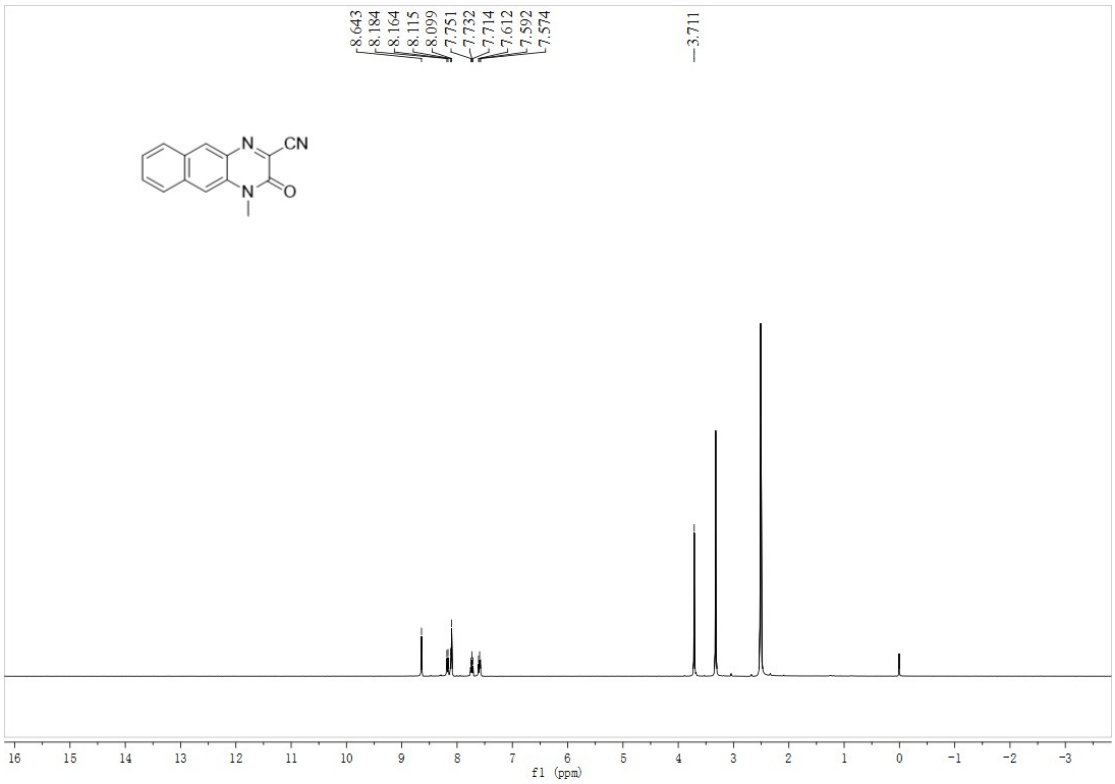
6,7-difluoro-4-methyl-3-oxo-3,4-dihydroquinoxaline-2-carbonitrile (3bo)

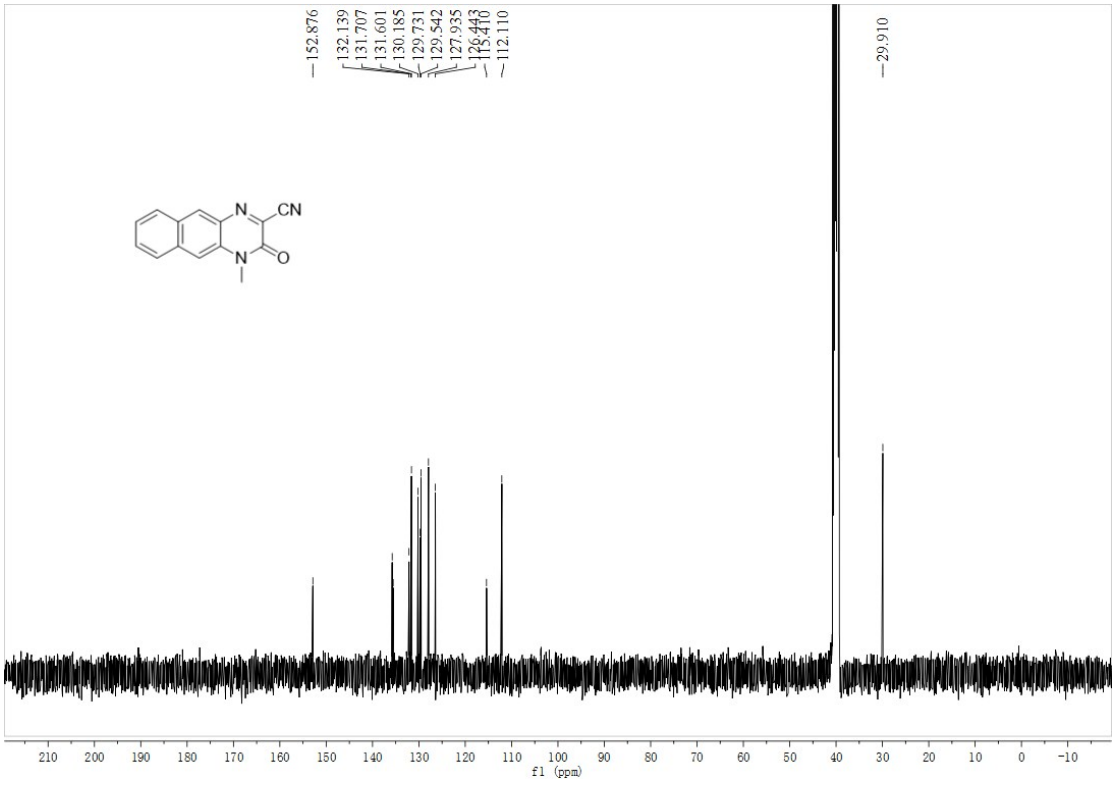

7.831
7.810
7.787
7.265
7.248
7.238
7.221
3.752
F
F
N
CN
N
O
f1 (ppm)


155.765
155.620
153.164
153.018
152.424
148.899
148.757
146.398
146.257
134.043
133.999
129.143
119.324
119.295
119.143
103.171
102.938
30.374
F
F
N
CN
N
O
f1 (ppm)

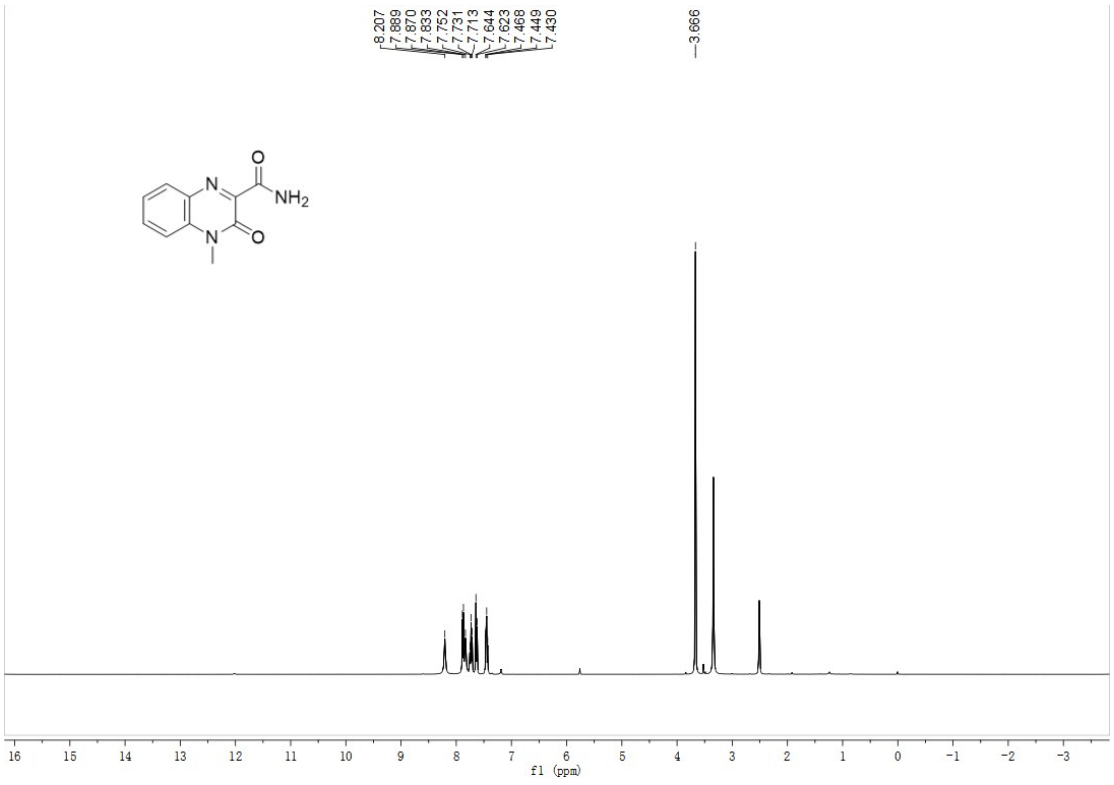


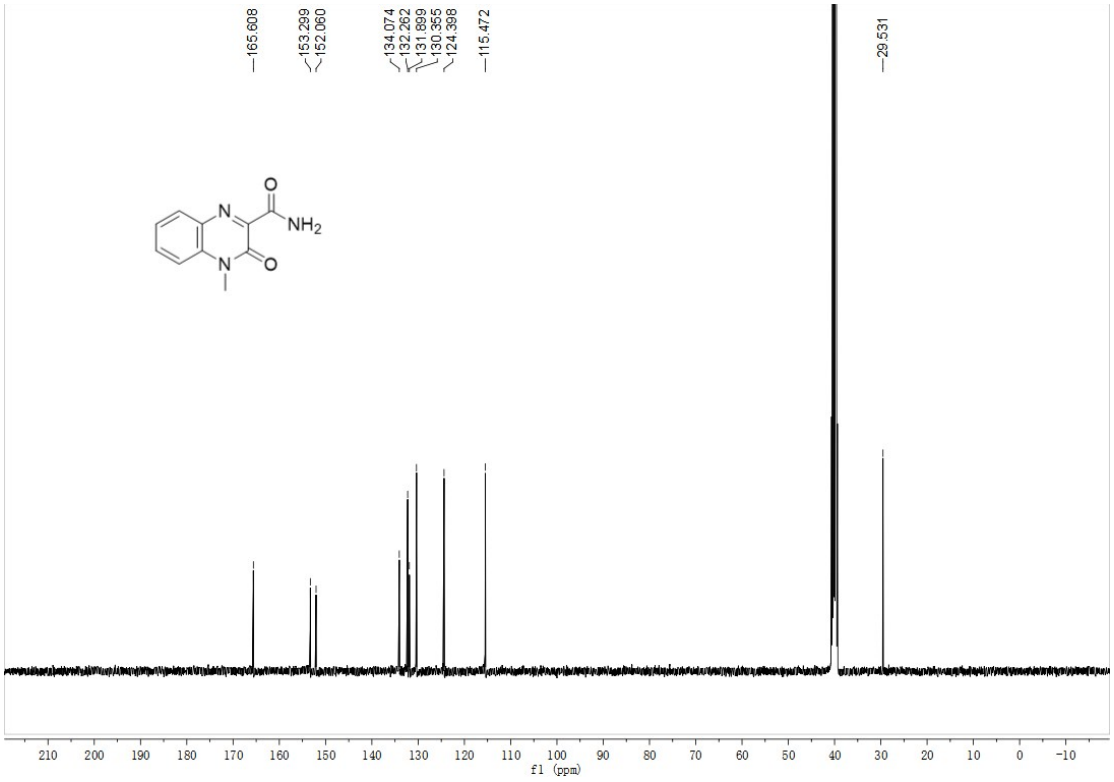
4-methyl-3-oxo-3,4-dihydrobenzo[g]quinoxaline-2-carbonitrile (3bp)


8.643
8.184
8.164
8.115
8.099
7.751
7.732
7.714
7.612
7.592
7.574
3.711
N
CN
N
O
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)


152.876
132.139
131.707
131.601
130.185
129.731
129.542
127.935
126.443
115.410
112.110
29.910
N
CN
N
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

4-methyl-3-oxo-3,4-dihydroquinoxaline-2-carboxamide (4)[2]




165.608
153.299
152.060
134.074
132.262
131.899
130.355
124.398
115.472
29.531
O
NH2
N
N
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)